Downloaded from orbit.dtu.dk on: May 05, 2023

DTU Library

Determination of the fraction of blowing agent released from refrigerator/freezer foam after decommissioning the product

Scheutz, Charlotte; Kjeldsen, Peter

Publication date:
2002

Document Version
Publisher's PDF, also known as Version of record

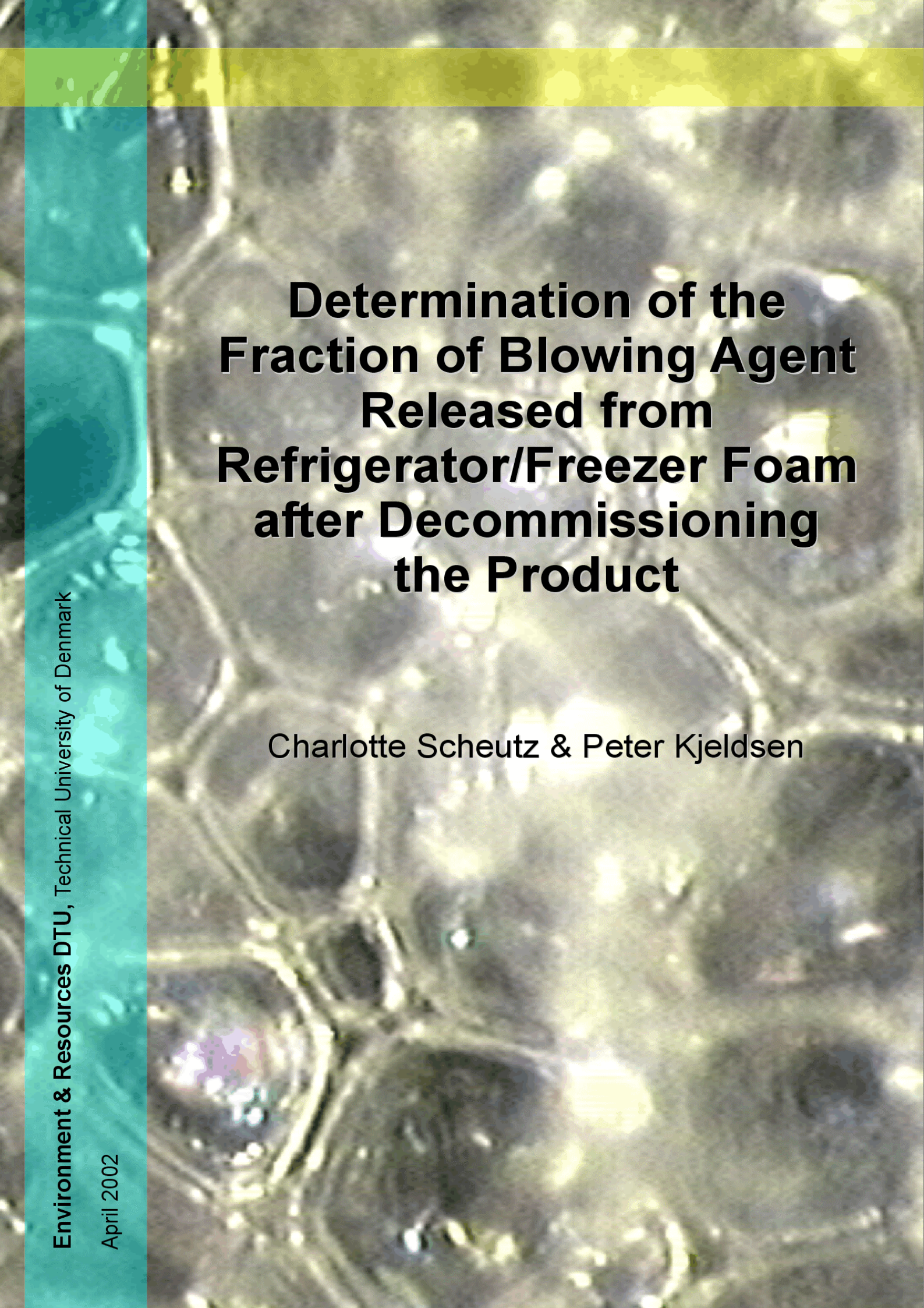
Link back to DTU Orbit

Citation (APA):
Scheutz, C., & Kjeldsen, P. (2002). *Determination of the fraction of blowing agent released from refrigerator/freezer foam after decommissioning the product*. Environment & Resources DTU. Technical University of Denmark.

General rights
Copyright and moral rights for the publications made accessible in the public portal are retained by the authors and/or other copyright owners and it is a condition of accessing publications that users recognise and abide by the legal requirements associated with these rights.

- Users may download and print one copy of any publication from the public portal for the purpose of private study or research.
- You may not further distribute the material or use it for any profit-making activity or commercial gain
- You may freely distribute the URL identifying the publication in the public portal

If you believe that this document breaches copyright please contact us providing details, and we will remove access to the work immediately and investigate your claim.



Determination of the Fraction of Blowing Agent Released from Refrigerator/Freezer Foam after Decommissioning the Product

Charlotte Scheutz & Peter Kjeldsen

Environment & Resources DTU, Technical University of Denmark

April 2002

DETERMINATION OF THE FRACTION OF BLOWING AGENT RELEASED FROM REFRIGERATOR/FREEZER FOAM AFTER DECOMMISSIONING THE PRODUCT

Charlotte Scheutz & Peter Kjeldsen

Environment & Resources DTU

Technical University of Denmark

April 2002

FOREWORD

Many home refrigerators are shredded after the end of their useful life. When this occurs, the insulating foam is reduced to fragments that may be incinerated or disposed of in a landfill. In the USA most of this is disposed of directly in landfills and very little is incinerated. The foam contains fluorocarbon compounds (blowing agents) such as CFCs, HCFCs or HFCs, which are strong greenhouse gases that contribute to global warming if released into the atmosphere. Relatively little information is available regarding the amount of blowing agent that escapes and how much remains in the foam after an appliance is shredded.

AHAM (Association of Home Appliance Manufacturers) is interested in data based on research in this area because many environmental assessments of household refrigerators assume that the entire blowing agent is released into the atmosphere when a product is shredded at end of its useful life.

The Appliance Research Consortium (ARC), which is an independent entity operated by AHAM has solicited bids on a research initiative, resulting in this research project.

Peter Kjeldsen and Charlotte Scheutz from Environment and Resources DTU, Technical University of Denmark, have carried out the project in the period February 1st to December 31st, 2001.

SUMMARY

The blowing agent (BA) for insulating foam used in appliances such as refrigerators and freezers is frequently a flourocarbon. Many appliances are shredded after the end of their useful life. When this occurs, the insulating foam is reduced to small pieces that often are disposed of in a landfill. Relatively little information is available regarding the amount of blowing agent that escapes and how much remains in the foam after an appliance is shredded. The escaped blowing agent may contribute to ozone depletion in the atmosphere or to the greenhouse gas effect. The objective of this study was to determine the fraction of blowing agent that escapes when a foamed refrigerator is shredded, and the amount released as a function of time during the following 6 weeks. Four different blowing agents were studied: CFC-11, HCFC-141b, HFC-134a, and HFC-245fa.

Two different methods have been used for determining the total content of blowing agent in foam, a method based on heating and a method based on extraction with dimethyl formamide. Initial investigations of the two methods showed that only one step is needed to get almost all (approx. 99%) blowing agent out of the foam sample. The heating method gives slightly higher total contents for all four blowing agents, is relative easy to use, and does not imply the use of large volumes of a toxic chemical as the extraction method does. The heating method is therefore to be preferred. Both methods as used in this project will probably underestimate the true total content of blowing agent in the foam panels due to an instantaneous loss of blowing agent while cutting the foam specimen out of the panel. Based on the instantaneous release experiments it is estimated that the total content determination is approximately 15% too low.

Four different methods have been used for measuring the releases of blowing agent from shredded foam. The methods are: a) Infinite bath experiment using gravimetric method measuring weight loss over time; b) Infinite bath experiment using extraction method measuring BA content in foam samples at different times; c) Batch experiment measuring BA release from foam specimen to closed volume over time; and d) Flux chamber experiment measuring BA flux from a container with foam specimens through which a constant gas stream is maintained. Comparing the gravimetric method to the other methods it was clearly shown that there was a poor correlation of the weight loss to the loss of blowing agent. This is probably a result of uptake of other gases (oxygen, nitrogen and water vapor) and the release of carbon dioxide which theoretically will be released with a higher rate than the BA. Thus, the gravimetric method cannot be recommended for measuring the BA loss from shredded foam. The extraction method uses large volumes of extraction fluids, and the precision of the method relies on that a large number of foam specimens are used. The batch method and the flux chamber methods are clearly of preference to the gravimetric and the extraction method. The flux chamber method gave the most reliable results, but is quite laborious. The batch method is simpler and gives a good representation of the BA mass released after shredding. However, the method seems to slightly underestimate the release. The reason for this has not been found.

The release experiments revealed that the BA release process from shredded foam conceptually can be divided into three phases: an instantaneous release (typical time frame in minutes), a short-term release (typical time frame of 250-500 hours for larger foam particles) and a long-term release. The release in the last phase is governed by closed cell diffusion. By

use of model simulations, the diffusion coefficients describing the short-term release were typically two orders of magnitude higher than the diffusion coefficients describing the long-term phase. The diffusion coefficients describing the long-term release were of comparable magnitude to closed cell diffusion coefficients reported in the literature from foam aging studies. The time frame of the long-term releases is highly depending on the particle size of the shredded foam. Model simulations showed that it will typically take 100 months to release 50% of the initial content in a foam particle with a diameter of 24 mm, but only 8 months for a foam particle with a diameter of 6 mm. This assumes that the particle keeps its diffusional properties after product decommissioning and disposal of the foam in a landfill.

The percentage of the BA foam content, which is instantaneously released, is generally increasing with decreasing particle size. For particles in the particle size range of 16 to 32 mm the instantaneous release is about 10% (w/w), increasing to about 40% (w/w) for particles in the range of 2 to 4 mm. Using data for typical size distributions for foam shredded in an industrial recycling facility for used refrigerators/freezers, the instantaneous release is estimated to be in the order of 17-24% (w/w). The short-term release seems also to depend on particle size with typical releases in the range of 3-15%.

Experiments with foams made by different producers indicated that the releases might vary significantly between producers. Foam blown with HFC-245fa showed losses between 6% and 24% after 6 weeks in experiments with foam panels from four manufactures. However the measured losses from manufacturer A, C, and D varied between 6-8%, while only foam produced by manufacturer B showed a much higher loss of 24%. It is therefore questionable whether manufacturer B is representative of panels blown with HFC-245fa in general. The same cannot be concluded for the experiment conducted with HFC-134a. The highest loss (15%) of HFC-134a was observed using foam from supplier B, but this was only slightly higher than the loss of 13% in experiment with foam from supplier D. The panels from manufacturers B and D seem more representative compared to manufacturer C, which showed a loss of 7%. It can therefore not generally be concluded that panels from manufacturer B overestimate the losses or are not representative. However, if the test foam panels truly represent the insulation foam used in freezer/refrigerators in the market this study shows that the loss of BA can vary between products.

Overall, the proportion of the BA content, which is released from foams within the first six weeks after shredding (i.e. including the instantaneous release) is in the order of 14-74%, depending on particle size (valid for a particle size range of 4 to 32 mm). The table below summarizes the magnitude of the releases. The numbers must be regarded as average values for all blowing agents studied.

The fractional distribution of the instantaneous and short-term releases as a function of foam particle size.

	Particle size category				
	<4mm	4-8mm	8-16mm	16-32mm	>32mm
Instantaneous release (%w/w)	40	34	18	10	5
Short-term release (%w/w)	60	40	10	4	2

The total BA released was 20-39% for typical size particles from Aarhus recycling facility. If the shredding leads to more coarse particle sizesthan at the Aarhus facility, the total release

will be lower. The remaining may be released slowly if the integrity of the foam particles with respect to diffusional properties is kept after disposal of the foam waste on landfills.

Based on the findings from the release experiments, the future yearly releases of the four blowing agents from decommissioning refrigerators/freezers in the United States was estimated for three different scenarios based on the particle size of the shredded material. For scenario A (smallest foam particles) almost all BA is released over a 50-year period (97.7%). For scenarios B and C the release over the 50-year period is 88.8% and 73.8% respectively and therefore a small but significant fraction of the release will take place after the 50-year period. The model assumes that all BA released from the foam particles is readily emitted, and does not take into account any attenuation of BA in the landfill or the soil covers surrounding the landfill, which may lead to reduced emissions.

CONTENTS

APPENDICES

1. INTRODUCTION

The blowing agent for insulating foam used in appliances (e.g., refrigerators and water heaters) and many building materials is frequently a flourocarbon such as HCFC-141b or HFC-134a. Prior to 1996 the most common blowing agent was CFC-11. New HFCs such as HFC-245fa are expected to be used extensively in the future. All of these compounds are strong greenhouse gases that contribute to global warming if released to the atmosphere.

Many appliances are shredded after the end of their useful life. When this occurs, the insulating foam is reduced to small pieces that may be incinerated or disposed of in a landfill. In the USA most of it is disposed of directly in landfills and very little is incinerated[1]. Relatively little information is available regarding the amount of blowing agent that escapes and how much remains in the foam after an appliance is shredded. Good data in this area is of interest because many climate change models assume 100% release at disposal.

Little is known about rates and time frames of the blowing agent release from foams especially after shredding and disposal of foam containing waste products. The blowing agent (BA) release is mainly controlled by slow outward diffusion from polyurethane (PUR). Theories for the CFC release from PUR foam have been developed by foam insulation research looking at the aging of the foams, i.e. the deterioration of the insulation properties of the foams due to diffusion of CFC out of the foam, and diffusion of atmospheric air into the foam[2, 3, 4, 5, 6, 7]. The CFC loss is governed by diffusion through the closed cell walls, and by simultaneous release of the fraction sorbed in the PUR. The diffusion in non-shredded foam boards is very slow, which means that experiments to measure diffusion coefficients are very time consuming if indirect methods are not used [2].

Recent laboratory studies[8] performed on PUR foam containing CFC-11 studying the distribution of CFC-11 in the foam and the short term releases after shredding showed that about 40% of the CFC is solubilized in the PUR phase, and that up to 10% of the total content will be released within a few weeks if the foam is shredded down to 2-cm sized pieces. For smaller pieces the short-term release will be larger. This study did not quantify the instantaneous release from cutting closed cells during the shredding process, so the numbers given above is excluding this release.

2. OBJECTIVES

The objective of this study is to determine the fraction of blowing agent that escapes when a foamed refrigerator is shredded, and the amount released as a function of time during the following 6 weeks. The objectives are met by performing laboratory experiments on cut foam cubes and foam particles obtained from realistic (i.e., comparable with industrial standards) shredding. Foam diffusion models[8] will be used for evaluating and extrapolating the results. The following blowing agents will be studied: CFC-11, HCFC-141b, HFC-134a, and HFC-245fa.

3. THEORY AND DATA EVALUATION

3.1 Basic theory.

The transport of gases in PUR foam is assumed to follow Fickian diffusion[5]. The gas composition as a function of time can be found by solving the diffusion equation for each compound [5]:

$$\frac{\partial C}{\partial t} = \nabla \cdot D_{eff,c} \nabla C \qquad (1)$$

Here C is the concentration depending on time (t) and position. $D_{eff,c}$ is the effective diffusion coefficient of the component in the foam (in m^2s^{-1}). Besides the diffusion equation with a known diffusion coefficient, we also need an initial distribution of the gas in the foam and the boundary conditions to be able to solve the equation.

The relation between the concentration of the compound in polymer material that surrounds a void, and the concentration of the compound in the void is supposed to be proportional as given by Henry's law[5]:

$$C_p = K \cdot C_g \qquad (2)$$

where C_p is the concentration in the polymer material (in mol·(m^3 polymer material)$^{-1}$), C_g is the concentration in the void (in mol·(m^3 gas)$^{-1}$), and K is the distribution factor (in (m^3 gas)·(m^3 polymer material)$^{-1}$).

3.2 Solutions to different geometries.

Specific solutions to Ficks second law (equation 1) depends on the size and geometry of the foam waste particles. Crank[9] compiled many solutions to Ficks second law, which were further elaborated by Grathwohl[10]. The solutions can be divided into two cases, the infinite bath, and the bath of limited volume. In the first case the CFC in the foam particle is released to a very large volume, which concentration can be assumed constant and independent of the release from the given particle. These solutions are valid for evaluating releases to the atmosphere, to containers with a considerable exchange of gas, or to the pore gas in a landfill where LFG continuously is produced. Solutions of the second case can be used for interpreting release experiments carried out in batch containers of limited volume. The diffusion coefficient is called D in the following equations.

For the *infinite bath* scenario the release from a spherical particle with the radius *a* is ($M_0 = C_0 \cdot V = 4\pi a^3 C_0/3$, where V is the volume of the sphere and M_0 is in g)[9]:

$$\frac{M_t}{M_0} = 1 - \frac{6}{\pi^2} \sum_{n=1}^{\infty} \frac{1}{n^2} \exp\left\{ - Dn^2 \pi^2 t / a^2 \right\} \qquad (3)$$

The equation for the flux out of the sphere, F_t (in g s^{-1}) is:

$$F_t = \frac{6 M_0 D}{a^2} \sum_{n=1}^{\infty} \exp\left\{ - Dn^2 \pi^2 t / a^2 \right\} \qquad (4)$$

For cylindrical foam particles the solution for spheres can be a quite good approximation. The following equation can be used for calculated the value for the term “a” to be used in the equations:

$$a = (\frac{3}{16} d^2 h)^{\frac{1}{3}} \quad (5)$$

where d is the diameter and h the height of the cylinder. For other geometrical shapes the following short-term approximations (only valid for the first release) can be used [10]:

$$\frac{M_t}{M_0} = 2\left(\frac{A}{V}\right)\sqrt{\frac{D \cdot t}{\pi}} \quad (6)$$

$$F_t = M_0\left(\frac{A}{V}\right)\sqrt{\frac{D}{\pi \cdot t}} \quad (7)$$

where (A/V) is the ratio of the external surface area of the particle to the volume.

3.3 Double compartment model

When foam is shredded or cut, a portion of the closed cells are destroyed. This will lead to an instantaneous release of the blowing agent from the fully opened cells. However, it is expected that some of the cell walls in the interior of the foam will be affected by the shredding/cutting, potentially leading to higher release rates from the affected part of the foam particle. It is assumed that the affected foam is evenly distributed in the particle, and that the release can be described by Ficks law as is the case for the intact foam.

The total content of blowing agent, M_0 in the particle is divided into two parts:

$$M_0 = M_{0,1} + M_{0,2} \quad (8)$$

where $M_{0,1}$ is the content in the affected (broken) fraction of the foam particle and $M_{0,2}$ is the content in the intact fraction of the foam particle. For both of the releases the first initial part of the release process, equation 6 and 7 can be used. This means that if the mass released, M_t is shown as a function of the square root to the time ($t^{½}$) the curve would be composed by two straight lines with different slopes, one for each of the release processes. By estimating $M_{0,1}$ and $M_{0,2}$ the governing diffusion coefficients for the two release processes, D_1 and D_2 can be calculated using the slopes of the lines.

The long-term release from a given foam particle can then be estimated using the calculated D_2 and equation 3.

4. LITERATURE REVIEW

4.1 Previous studies on release of blowing agent from insulation foam (diffusion coefficients reported in literature)

Some studies are reporting diffusion coefficients for air components and different blowing agents in the literature. Nearly all reports are based on aging studies where the diffusion coefficients reflect the long-term releases.

Very few data on the foam diffusion coefficient of CFC-11 has up to the present been obtained by direct permeability measurement because of the very long time needed to achieve steady state. Table 4.1 shows the diffusion coefficients for the different blowing agents studied in this project with the addition of HCFC-22 in PUR foam based on literature data. Due to the very long time needed for measuring the diffusion coefficient directly, some values are calculated using the following equation based on determination of the diffusion coefficient, D_p, in rigid PUR:

$$D_{eff,c} = \frac{D_p \cdot (l/d)}{f_g + K(1-f_g)} = \frac{1}{K} \cdot D_{eff,p} \qquad (9)$$

where D_p is the diffusion coefficient in the solid polymer material (in m^2s^{-1}), f_g is the void volume fraction of the foam, and $D_{eff,p}$ is the diffusion coefficient in the differential equation with the pressure as the depending variable. The geometrical factor (l/d) in the equation can be estimated from the porosity of the foam using the equation (7):

$$l/d = \frac{1}{1-f_g} \qquad (10)$$

The equation assumes that all the polymer material in the foam is present in the cell walls, and therefore slightly overestimates the thickness of the cell wall.

A rapid steady-state measurement technique has also been used in a single case[2]. Here the steady state conditions (i.e a constant concentration gradient through the foam sample) achieved prior to the measurement was obtained by increasing the temperature of the sample, which significantly increases the diffusion process. The technique gave reproducible results for gases like O_2, CO_2 and N_2, however for CFC-11 the reproduction was somewhat lower.

The distribution factor, K is also contained in equation 3. This value was determined for CFC-11 by Bart and du Cauzé de Nazelle[5] on milled foam samples measuring the total mass change of the foam sample after equilibrium was settled. Their determined value was 10.0. Recently, Hong and coworkers determined a K-value by sorption experiment on micrometer thin PUR slices[6,11]. They also measured the polymer diffusion into very thin slices of rigid PUR (slice thickness of about 7 μm) and determined the polymer diffusion coefficient, D_p. The use of very thin slices made it possible to measure the diffusion coefficient, D_p over a reasonable time frame. For CFC-11, they observed that D_p decreased with decreasing CFC-11 concentration.

Table 4.1. Distribution coefficients and diffusion coefficients of different blowing agents in PUR foams obtained from literature. The values are valid for 25°C.

Reference	K (m^3 gas/m^3 PUR)	D_p ($10^{-16} m^2 s^{-1}$)	$D_{eff,p}$ ($10^{-14} m^2 s^{-1}$)	$D_{eff,c}$ ($10^{-14} m^2 s^{-1}$)
CFC-11				
Brandreth and Ingersoll[2]	-	-	-	1.3[a]
Ostogorsky and Glicksman[4]	-	-	22-57[b]	0.6-1.7[c]
Bart and du Cauzé de Nazelle[5]	-	0.01	6.0	0.18[c]
Hong and Duda[6]	30-39	8-10		2.8-3.2[a]
Kjeldsen and Jensen[8]	30-37	-	-	-
Khalil and Rasmussen[18]	-	-	-	0.05-0.23[d]
Dement'ev et al.[12]	-	-	-	12
Fan and Kokko[13]	-	-	-	4.6
HCFC-22				
Hong and Duda[6]	10	35	-	14.8[a]
HCFC-141b				
Wu et al.[14]	-	-	-	19
Hong and Duda[6]	49	12	-	3.0
HFC-134a				
Hong et al.[11]	4.8	8.1	-	3.8
HFC-245fa				
Wu et al.	-	-	-	3.9
Hong et al. [11]	20	2.8	-	1.0

a: values of $D_{eff,c}$ obtained by measurement of D_p and calculating $D_{eff,c}$ using equation 9 and 10 as described in the text with a gas-filled porosity, f_g, of 0.98.

b: values obtained by steady state measurements on foam samples

c: calculated using equation 9 (last part) and a K-value of 33 as determined as the average value determined by Hong and Dudas[6] and Kjeldsen and Jensen[8]

d: Based on re-evaluation by Kjeldsen and Jensen[8]

Table 4.1 shows that observed PUR foam diffusion coefficients for CFC-11 are in the range of $0.05–12 \cdot 10^{-14}$ $m^2 s^{-1}$. The magnitude probably depends on the foam type (i.e. the real geometric factor to be used in equation 3, and on the method used. Directly determined values may be relatively higher than the values calculated by use of equation 3, because some open cells are introduced by cutting the foam sample[4].

One study used a gravimetric approach to determine the diffusion coefficients for CFC-11 and HCFC-22[15], and found diffusion coefficients of $0.8\text{-}1.5 \cdot 10^{-12}$ $m^2 s^{-1}$ and $0.3\text{-}1 \cdot 10^{-12}$ $m^2 s^{-1}$ for CFC-11 and HCFC-22, respectively. These values are much higher than the numbers given in Table 4.1. To our opinion the diffusion coefficients given represent the short-term release, since their experiments were only run for a relatively short period.

Only one release experiment has looked at the initial release from shredded or demolished foam[8]. This experiment was carried out at the Technical University of Denmark. Here diffusion coefficients for the short-term release were determined for CFC-11, and the values were in the order of $2\text{-}20 \cdot 10^{-12}$ $m^2 s^{-1}$.

4.2 Current foam recycling/recovery techniques used in the world today

According to Article 16 of the "Regulation (EC) No 2037/2000 of the European Parliament and of the Council of 29 June 2000 on substances that deplete the ozone layer", all member states shall control substances contained in refrigeration, air-conditioning and heat pump equipment. As of December 31, 2001, this also includes controlled substances in domestic refrigerators and freezers. Article 16 further states that Member States are expected to “take steps to promote the recovery, recycling, reclamation and destruction of controlled substances and assign to users, refrigeration technicians or other appropriate bodies responsibility for ensuring compliance“. Member States are also expected to “define the minimum qualification requirements for the personnel involved”. Furthermore, by 31 December 2001 at the latest, Member States should have reported to the Commission on the programmes related to the above qualification requirements. The Commission shall evaluate the measures taken by the Member States. In the light of this evaluation and of technical and other relevant information, the Commission, as appropriate, shall propose measures regarding those minimum qualification requirements. Member States should have reported to the Commission by 31 December 2001 on the systems established to promote the recovery of used controlled substances, including the facilities available and the quantities of used controlled substances recovered, recycled, reclaimed or destroyed.

However, most EU countries have as of February 2002 not yet reported the required information to the Commission. Based on our contacts to the national bodies of the various EU countries, it is our impression that there is a rather limited knowledge available in these countries as to the handling of CFC gasses from freezer/refrigerator insulating foam. This situation is expected to improve during the first half of 2002, with the EU countries working out the reports required by the Commission.

In order to establish a status over foam recycling/recovery techniques used in the world today a questionnaire was send out to all EU members of the management Committee operating under Article 18 of Regulation EC2037/00. The questionnaire is attached as appendix 11. EU member-states include Austria, Belgium, Denmark, Finland, France, Greece, Germany, Italy, Ireland, Luxembourg, Netherlands, Portugal, Spain, Sweden, and United Kingdom. In spite of several reminders only five member states responded on the questionnaire: Denmark, Sweden, Germany, Netherlands, and Ireland.

It is our impression that mainly countries that have already implemented regulations that cover not only CFC in cooling circuits but also the handling of CFC in foam in freezers/refrigerators responded on the questionnaire. This is based on telephone interviews with employees of the Danish EPA and Århus Recycling Company. However, there is intense focus on the area, through EU regulations and legislation, which demand that all CFC in refrigerators and freezers (including the foam) should be recovered for destruction or recycled, thus implying the need to develop and implement new technologies in the very near future.

Table 4.3. Current situation on foam recycling/recovery techniques used in five European countries today

Country	Foam recycling/recovery techniques	Recycling facilities
Denmark	Crushing of R/F in a sealed facility→treatment of exhaust air stream by catalysis →HCl/HF + shredded foam (incineration)	Dansk Genindvinding
Sweden	Shredding in closed units→ collection of air→ treatment of exhaust air stream by condensation→CFCs + shredded foam (incineration)	Bjästa Återvinning Stena Bilfragmentering Svensk Freonåtervinning
Germany	Crushing of R/F in a sealed facility→separation of PU foam→pore and matrix degasification→condensation of exhaust air→ CFC (purity 99,9%) + shredded foam (incineration +landfill)	25 special facilities for handling used freezer/refrigerators
Netherlands	Shredding of R/F→ degasification→(H)CFCs incineration. 100% reuse of degassed foam (powder) as adsorption material – after reuse it goes to a cement kiln for incineration	Coolrec (facilities in Einhoven and Dordrecht)
Ireland	No recovery of CFCs in insulation foam in R/F. Residue (including foam) from iron and steel recovery plants are landfilled	

Denmark, Sweden, Germany, and Netherlands all had regulations that covered handling of insulation foam in F/R before December 31, 2001.

5. LABORATORY EXPERIMENTS AND METHODOLOGY

5.1 Chemicals

The CFC-11, HFC-134a, HCFC-141b, and HFC-245fa used were all obtained in high purity. CFC-11, HFC-134a, HFC-245fa were obtained from Interchim, France while HCFC-141b was obtained from Honeywell, Netherlands. The chemicals were mainly used for calibration and control experiments. N,N-Dimethylformamide (DMF) was obtained from Merck, Germany. DMF was used for extraction of foam samples. Table 5.1 lists physical and chemical properties of the blowing agents included in this study.

Table 5.1. Physical and chemical properties of CFC-11, HFC-134a, HCFC-141b, and HFC-245fa.

Chemical name	**Unit**	**Trichlorofluoro methane**	**1,1,1,2-tetra-fluoroethane**	**1,1-dichloro-1-fluoroethane**	**1,1,1-trifluoro-3,3-difluoro-propane**
Synonyms		CFC-11	HFC-134a	HCFC-141b	HFC-245fa
Structure		CCl_3F	CH_2FCF_3	CCl_2FCH_3	$CF_3CH_2CHF_2$
CAS no.		000075-69-4	000811-97-02	001717-00-6	460-73-1
Molecular weight	g/mol	137.37	102.03	116.95	134.05
Boiling point	°C	23.8	-26.2	32	15.3
Vapor pressure	mmHg	802.8	430	707	1.24bar
Water solubility	mg/L	1100	67	2632	n.d.f
Log K (octanol-water)		2.53	1.68	2.37	n.d.f
Saturated gas concentra-tion	g/L (1atm, 25°C)	5.62	4.17	4.78	5.48
Ozone depletion potential		1.0	0	0.15	n.d.f
Halocarbon global warming potential		1.0	0.26	0.15	n.d.f

n.d.f: no data found

5.2 Foam samples

Foam samples blown with four different blowing agents (CFC-11, HCFC-141b, HFC-134a, HFC-245fa) were included in this study. Experiments with these four blowing agents were in general carried out in parallel.

The ARC Monitoring committee supplied foam panels blown with three different blowing agents (HCFC-141b, HFC-245fa, and HFC-134a). The foam panels were 2 ft. square by 2 in. thick, encased in aluminium foil. The foam panels were produced in late 1997 by the same manufacturer (in this project referred to as manufacturer B).

PUR foam samples containing CFC-11 were obtained from a used refrigerator. Details of the refrigerator are given in Table 5.2 (column A). Foam samples were taken different places from the refrigerator door. The door was homogenous without shelves, or storage boxes, etc. Samples were taken by first removing a part of the plastic casing, then cutting out samples using a cork bore. The remaining holes were closed by vapor-tight tape.

Table 5.2. Description of the sampled refrigerators

Refrigerator	**A**	**B**
Type	Refrigerator	Combined refrigerator and freezer
Brand	Zanussi	Atlas
Model	SL 1201 F	AFK 125
Prod. No.	B 1141	9240452
Series no.	77C 10404523	207-0099
Country of production	Italy	Sweden
Year of production	1977	Between 1972-1974
Blowing agent	CFC-11	CFC-11
Samples	Door (which is homogenous - without shelfs and boxes)	Side (mid)
Experiments conducted	Included in all experiments in paralelle with foam blown with HCFC-141b, HFC-134a, and HFC-245fa.	Only included in flux chamber experiment using shredded material.

In one experiment samples of foam blown with HFC-245fa produced by four different manufacturers were included. The foam panels were 2 ft. square by 2 in. thick encased in aluminum foil. Four different manufacturers produced the foam panels in late 1997. In this report the manufacturers are referred to as A, B, C, and D.

Experiments were carried out with shredded foam. An older combined refrigerator and freezer was shredded in Aarhus Recycling Company. Details of the refrigerator used in this experiment are given in Table 5.2 (column B). The total amount of blowing agent in the foam before shredding was determined by taking smaller foam samples from the refrigerator. Foam samples were taken from the side cabinet (mid) using sharp metal tubes. The foam samples were sealed and kept in the metal tubes until analysis. Shredded material was collected at the exit of the shredding unit and kept in gas-tight bags at low temperature until arrival at the laboratory. In addition, a larger foam quantity was collected in order to determine the size distribution of the shredded foam.

In general, samples were taken by cutting out a larger piece ($10 \cdot 10 \cdot 5$ cm^3) of foam from the test panels. After removing the aluminum foil, smaller foam samples were cut out from the center of the large foam sample using a cork bore. To avoid further loss of BA from the foam panels during storage after cutting out samples they were sealed by vapor-tight tape. In order to compare results from different experiments, foam samples generally had the same shape and size, i.e., a cylinder with a diameter of 1 cm and a height of 1 cm.

5.3 Methods used for measuring the total content of blowing agent in polyurethane

The total content of blowing agent in polyurethane foam was determined using two different methods; one based on heating and one based on solvent extraction.

5.3.1 Determination of the total content of blowing agent in polyurethane by heating

A core foam sample (dia.=1 cm) was cut out from the center of the foam panel with a sharp cork bore. The core sample was measured using a electronic slide gauge, weighed, and placed in a 115 mL glass bottle which was sealed with a Teflon coated septa and an aluminum cap. To release the halocarbons from the foam the bottle was incubated in an oven for 48 hours at 140°C. When cooled down to room temperature gas samples were redrawn from headspace and analyzed by gas chromatography.

An experiment was performed to demonstrate the effectiveness of the heating procedure to drive out the halocarbons. Four separate foam core samples were subjected to four successive heating cycles. After GC analysis between each cycle, the bottle was opened and the headspace flushed with air to remove the halocarbons and the sample reheated for 48 hours at 140°C. The test showed that at least 99% of the halocarbons were driven out in the first heating step (results shown in Appendix 3).

5.3.2 Determination of the total content of blowing agent in polyurethane by solvent extraction

A core foam sample (dia.=1 cm) was cut out from the center of the foam panel with a sharp cork bore. The core sample was measured, weighed, and placed in a glass vial containing 15 ml N,N-Dimethylformamide (DMF). The foam samples were extracted for 72 hours. A sufficient extraction time was determined in an experiment where liquid samples from the same extract were taken every day for five days. The test showed no change in concentration after one day, indicating that no further extraction took place after 24 hours. The extracts were diluted in DFM before analysis on gas chromatograph.

A test similar to the heating experiment was performed to study the effectiveness of the solvent to extract the halocarbons contained in the foam matrix. Four separate foam core samples were extracted four times each. After sampling of the liquid phase, the solvent was replaced by new solvent and left for 72 hours before a new sample was taken (results shown in Appendix 4).

The test using four extraction steps showed that at least 99% of the halocarbons were extracted in the first step (results shown in Appendix 4).

5.4 Gas Chromatographic Analysis

5.4.1 Gas chromatographic analysis of halogenated compounds

Gas chromatography (GC) was performed by direct on-column injections of either gas or liquid samples. For analysis of gas samples 10-500 µl gas was injected manually via an inlet to a gas chromatograph, while for liquid samples 1-5 µl was injected by an auto sampler model A200S. The halogenated compounds were measured on a Carlo Erba HRGC 5300 gas chromatograph equipped with an electron capture detector (ECD) and a flame ionization detector (FID) in parallel. The FID is mainly used for analysis of HFC-134a since the sensibility on the ECD for this compound was very low. Samples were injected on a WCOT fused silica capillary column (CP-Sil-19 CB) with nitrogen being the carrier gas. The

compounds were analyzed with an isotherm column temperature of 40°C. When liquid samples were injected the temperature was raised to 220°C in order to get the solvent out of the column. Concentrations of the target compounds were calibrated by injection of gas standards (no fewer than 12 concentration levels) and constructing a standard curve. Calibration standards were made by adding a specific volume of a saturated pure gas at atmospheric pressure to a known volume of air. The standard curves were not linear throughout the whole concentration range. However in general samples were within the linear part of the standard curve - samples with higher concentrations were diluted. Gas chromatograph conditions for analysis of halocarbons are shown in Table 5.3.

5.4.2 Gas Chromatographic Analysis of CO_2

Carbon dioxide was analyzed on a Chrompack Micro GC CP-2002P gas chromatograph equipped with a thermal conductivity detector and two columns. Carbon dioxide was quantified on a 10 m long Poraplot Q column. Carbon dioxide concentrations were calibrated by analysis of standard gasses and construction of a standard curve. The lowest standard was 200 ppm (=0,02%vol.). The carrier gas was helium and the column temperature was 40°C.

Table 5.3 Gas chromatograph conditions for analysis of halocarbons

Compound	Detector	Ret.	Highest	Lowest	Detection	Relative sensibility
CFC-11	ECD	1.662	0.4	0.008	0.1	High
HFC-134a	FID	1.098	800	18.0	100	Low
HCFC-141b	ECD	1.853	8	0.02	1.0	High
HFC-245fa	ECD/FID	1.307	220	0.4	10	Medium

5.5 Compression test

The density of the four foam samples was measured by weighing cylinders (diameter = 2.0cm and height = 2.5cm) cut out of the foam panels. Four replicates of each sample were included.

To measure the amount of blowing agent dissolved in the polymer, foam cylinders (diameter=2.0cm and height 2.5cm) were compressed by a 60 tons press (Model Mohr & Federhaff AG, Mannheim, Germany (600kN). The foam samples were compressed with 15 tons (or 370 MPa). The foam cylinders were measured using an electronic slide gauge and weighed before and after compression and the volume of the PUR material was calculated (assuming that the compression has fully removed the gas phase). The content of blowing agent in the compressed (M_f in g) and uncompressed (M_s in g) foam samples were analyzed using solvent extraction method. A distribution coefficient K describing the distribution of blowing agent between the gas- and the polyurethane phase can be calculated (assuming that the content of blowing agent in the compressed samples equals the blowing agent sorbed in the PUR material) with the equation:

$$K = \frac{f_g \cdot M_f}{(1 - f_g) \cdot (M_s - M_f)} \qquad (11)$$

where f_g is the void volume fraction of the foam.

Gas-filled porosity was calculated based on the density measurements using a density of solid PUR of 1240 g/L and densities of BA gas in the voids calculated using an assumption of 25°C and 1 atm.

$$f_g = \frac{\rho_{foam} - \rho_{b.solidPUR}}{C_{BA0} - \rho_{b,solidPUR}} \cdot MW_{BA} \quad (12)$$

where ρ_{foam} is foam density mg/cm^3

$\rho_{b,solid\ PUR}$ is the density of solid PUR (1240 mg/cm^3)

C_{BA0} is the density (concentration) of BA in the void space (1 atm. and 25°C)

MW_{BA} is the molecular weight (g/mol)

The calculated gas-filled porosity was compared with the measured porosity based on the results from the compression test.

5.6 Size distribution analysis of shredded material

The particle size distribution of the shredded material was determined using standard soil sieves. The following meshes were included: 1 mm, 2 mm, 4 mm, 8 mm, 16 mm, and 32 mm. Before sieving, plastic parts were hand separated from the shredded foam sample. Two samples (50 g) of shredded material were sieved. Pictures of the shredded foam are shown in Appendix 5.

6. FOAM CHARACTERISTICS

6.1 Characteristics of foam samples used in release experiments

Table 6.1 shows the characteristics of the four foam panels. The densities found (and calculated gas porosities) are within the range expected for PUR foams[3,16]. The volume reduction of the foam samples after compression was in the range of 0.92 to 0.96, which is a bit lower than the calculated gas porosities of 0.97 - 0.99. The volume reduction was measured after the compression was over, and it is likely that the value under compression was slightly higher. The total content of BA in foam is for CFC-11, HCFC-141b, and HFC-245fa in the range of 11.6 to 13.3 %w/w, which is close to the expected values which are in the range of 10-15 %w/w [17, 18, 19]. The foam panel blown with HFC-134a is in the lower end with a total content of 7.0 %w/w. Total amounts given in Table 6.1 were measured by the heating method. All results are shown in Appendix 1.

Carbon dioxide is always formed during the foam manufacturing process, and is therefore always present as a co-blowing agent. The initial content will vary depending on the production conditions. Carbon dioxide will diffuse more rapidly out of the foam due to its higher diffusion coefficient compared to the BAs. The diffusion rates are greatly influenced by foam properties, gas partial pressures, temperature, and the presence of diffusion barriers like outer casing of the foam. The total content of carbon dioxide in the four foam samples was in the range of 0.14 to 1.5 g/L. The total content of carbon dioxide is shown in Table 6.1. The foam blown with HFC-134a contains a large amount of carbon dioxide. This could be the result of a high initial content due to the conditions during foam processing or a low loss during storage due to a higher density than the other foams. Diffusion barriers such as high density slow down the diffusion processes causing a low outward diffusion of carbon dioxide [20]. The foam blown with CFC-11 contains less carbon dioxide, which is expected since it is the oldest foam, produced in 1977.

During the production of PUR (spraying process) an exothermic reaction increases the foam temperature to a maximum of 130°C to 160°C. BA gas pressure, which is equal to 1 to 1.05 atmospheres at the peak temperature, is then reduced to about 0.75 atmosphere when the foam cools down to the ambient temperature[12]. Subsequently, part of the BA enters the polymer matrix reducing the cell gas pressure. The amount of BA in the polymer matrix will depend on the solubility of the BA in the PUR. Solubility is determined by the degree of similarity between the force field of the permeating molecule and that of the polymer molecule [21].

The amount of BA dissolved in the polymer was measured by compression, assuming that the amount in the compressed foam sample consists only of the fraction sorbed in the PUR. The amount of BA dissolved in PUR varied between 23% to 30%. The calculated distribution coefficients (K-values) of 10–25 were slightly lower than the values reported in the literature (see Table 4.1).

Swanström & Ramnäs[20] found that approximately half of the total content of CFC-11 in the foam was dissolved in the polymer in 10–20 years old foam samples. However a significant variation in BA solubility has also been observed in a study performed by Bomberg & Kumaran[23]. Samples taken from different foams showed a total content of CFC-11 in the range of 10 to 12.2 %w/w. However, the distribution of the BA between the cell gas and the polymer showed large variations: from 22% up to 60% of the CFC-11 was dissolved in the

polymer. In another study by Bomberg & Brandreth[24] foam samples showed that around 70% of the CFC-11 was in the cell gas after 11 years of laboratory storage. Another foam sample showed that a reduction of 54% in the cell gas took place within a few weeks after manufacture.

Table 6.1. Measured and calculated parameters for the four foam panels

Parameter	**Unit**	**Blowing agent**			
		CFC-11	**HFC-134a**	**HCFC-141b**	**HFC-245fa**
Density, ρ_{foam}	g/L	24.6	39.0	32.2	30.7
Porosity, f_g *(calculated)*		0.985	0.972	0.978	0.980
Porosity, f_g *(measured)*		0.964	0.929	0.919	0.933
Total content of BA a)	g/L	3.43	2.78	3.77	3.66
	% w/w	13.3	7.0	11.6	11.6
Total content of CO_2	g/L	0.14	1.50	0.75	0.48
	% w/w	0.58	3.86	2.34	1.61
Fraction of CO_2 b)	% w/w	3.9	35.0	16.6	11.6
Content of BA in polymer	g/L	1.01	0.63	1.05	0.91
Fraction sorbed in PUR	%	29.5	22.7	27.8	24.8
Distribution coeff., K	m^3 gas· $(m^3$ PUR$)^{-1}$	24.6	10.1	16.5	14.9

a): as measured by the heating method

b): calculated as $M_{CO2}/(M_{CO2}+M_{BA})$

6.2 Size distribution of shredded foam from Aarhus Recycling Facility

Table 6.2 shows the results of the size distribution analysis. Two sub-samples A and B (approx. 50 g) of shredded material were analyzed. The size distribution is shown as foam fractions in different size intervals both by weight and in percentage. A substantial part (> 40%) of the foam particles are between 8-16 mm and the main fraction (> 59%) is in the range of 8 – 32 mm.

Table 6.2. Size distribution of shredded foam particles from actual Danish shredder.

Foam sample	**A**		**B**	
Size	**Foam**	**Fraction**	**Foam**	**Fraction**
mm	**g**	**% w/w**	**g**	**% w/w**
< 1	5.0	9.7	1.6	3.5
1 to 2	2.0	3.9	0.2	0.3
2 to 4	4.0	7.8	0.6	1.3
4 to 8	10.2	19.7	4.6	10.0
8 to 16	22.1	42.9	24.9	54.5
16 to 32	8.2	15.9	13.9	30.4
Total	51.5	100	45.7	100

7. INFINITE BATH EXPERIMENT

The objective of the infinite bath experiment is to quantify the release of BA from foam particles. In the infinite bath experiment the release of BA is examined under maximal concentration gradient, since the blowing agent is released into a infinite air volume where the concentration of BA can be assumed to be zero. To evaluate the release of blowing agent from foam, well-defined foam samples were carefully cut and placed on a wire frame at room temperature. Two different approaches were tried out: the gravimetric method, were the weight of the foam sample is measured over time, and a solvent extraction method, where the total amount of blowing agent left in the foam is measured over time.

The gravimetric method is quick, cheap and non-destructive and therefore of preference. If this analytical method could be used to quantify the release of blowing agent, several experiments could be performed within the time and economical constraints of the project. However, the success of the gravimetric method depends on the kinetics of the releases of co-blowing agents (such as CO_2) and the uptake kinetics of atmospheric air components (N_2, O_2, and water vapour). The comparison of the molar weight of the gases in question, and the fact that the diffusion coefficients of the gases in the open pores (introduced by shredding) are different, indicates that there may be difficulties with using the gravimetric method for quantification of the CFC/HCFC/HFC releases. To evaluate the precision of the gravimetric method for quantifying the releases another experiment based on solvent extraction was carried out.

The solvent extraction method is destructive because foam samples are extracted individually over time. The success of this method depends on the possibility of obtaining foam particles of the same size (volume) and that share the same properties, e.g., homogenous distribution of BA. The deviation of the BA analysis must be lower than the deviation between the sizes of the cut foam particles and the deviation between the content of BA in the cut foam particles.

7.1 Quantification of the release of blowing agent from foam by the gravimetric method

In order to evaluate the gravimetric method 75 foam cylinders (diameter=1cm and height=1cm) were placed on a frame in atmospheric air at room temperature. The cylinders were weighed (together incl. the frame) over time on an analytic balance (1/1000-g). The experiment was run for approximately 17 weeks (2500 hours). Experiments were carried out with four foam types blown with four different blowing agents (CFC-11, HCFC-141b, HFC-134a, and HFC-245fa). A control experiment were the weight of a metal weight was measured was carried out in parallel. Figure 7.1 shows the measured weight of foam blown with four different blowing agents as a function of time. In order to compare the results from different foam types the total range of the weight scale on the graph is 0.05 g with a minor unit of 0.01 g. Figure 7.1 shows the results.

The foam blown with CFC-11 and HFC-245fa shows a continuous weight loss throughout the whole period (2500 hours). For both compounds the weight loss seems to decline after 400 hours – more pronouncedly for HFC-245fa. However in the experiments with foam blown with HFC-134a and HCFC-141b we observed an increase within the first 100 hours followed by a decline in the weight – more pronounced for HFC-134a. The weight gain is believed to be a result of uptake of moisture, oxygen and nitrogen from air. Uptake of air components will

thus underestimate the release of blowing agent from foam. However cell gas analysis showed that the foam also contains CO_2 and therefore a weight loss is not only due to loss of blowing agent, but also CO_2, which will diffuse rapidly out of the foam. If the foam contains CO_2, using the gravimetric method will overestimate the loss of blowing agent. One study examined desorption of HCFC-22 from foam slides using a gravimetric method[15]. In one experiment they observed a weight gain in the initial period, which they attributed to air saturation of the foam.

Independently of foam type we observed three periods where we measure a minor weight gain (after 500, 1100, and 1500 hours). Since the control experiment does not show this tendency the weight gain can't be explained by instability in the analytic balance.

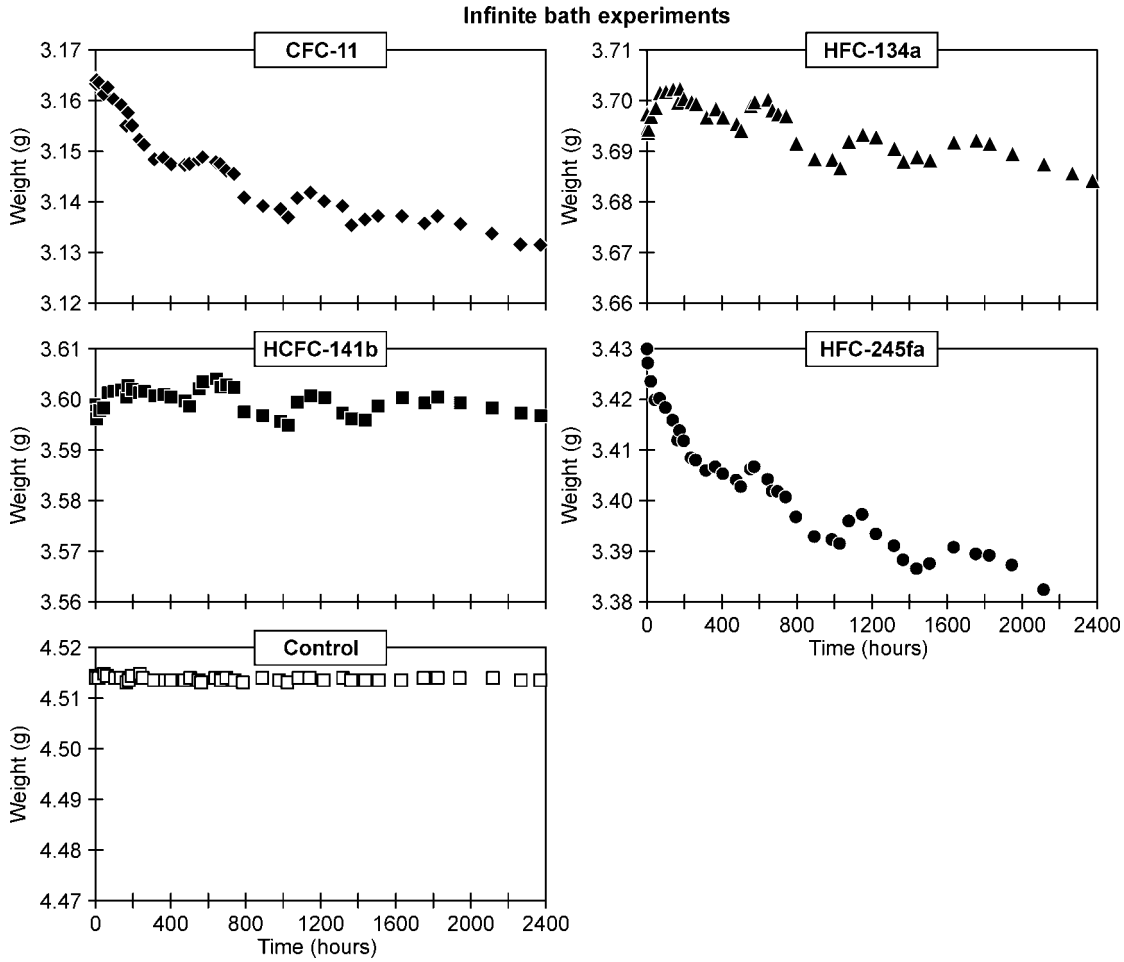


Figure 7.1. Measured weight loss from foam blown with four different blowing agents as a function of time.

The total loss of BA in percentage can be calculated using the measured weight loss results and the initial total content of BA in the different foams. Figure 7.2 shows the total loss in percentage by weight for foam blown with four different blowing agents as a function of time. Figure 7.2 shows that the total loss of CFC-11 and HFC-245fa after 2500 hours is approximately 10% and 15% respectively. The total loss of HFC-134a sums up to 3% after 2500 hours while the foam blown with HCFC-141b shows almost no loss (1%) at the end of the experiment period. The calculation is based on the assumption that the weight reduction is

only due to loss of blowing agent. Since analysis showed that all the foams contain carbon dioxide, the calculated loss based on weight will overestimate the loss. Since carbon dioxide tends to diffuse more rapidly out of the polymer matrix one might expect a higher weight loss from foam with high carbon dioxide contents compared to foam with lower carbon dioxide contents. However, since HFC-134a and HCFC-141b contain more carbon dioxide compared to CFC-11 and HFC-245fa this does not explains the results obtained. The foam blown with HFC-134a and HCFC-141 seems to be stronger adsorbent of moisture compared to CFC-11 and HFC-245fa. Based on this experiment it can't be concluded whether the release of BA is much higher from foam blown with CFC-11 and HFC-245fa compared to HFC-134a and HCFC-141, or whether the observed differences are more a result of the difference between the foams as moisture adsorbents. Based on these findings it can be concluded that the gravimetric method is not accurate enough for quantification of the CFC/HCFC/HFC releases.

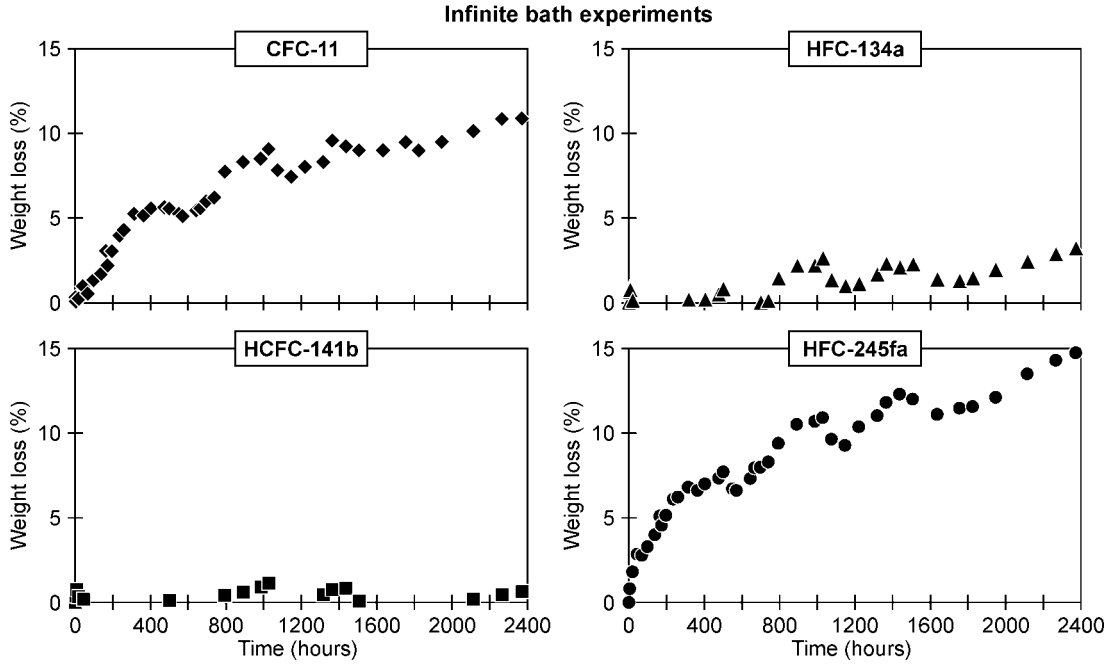


Figure 7.2. Measured weight loss in percentage from foam blown with four different blowing agents as a function of time.

7.2 Quantification of the release of blowing agent from foam by solvent extraction.

75 foam cylinders (diameter=1cm and height=1cm) were placed on a frame at room temperature. Three cubes were withdrawn from the tray at different times and extracted individually in N,N-Dimethylformamide, followed by GC-analysis. Extracts from the extracted foam cylinder were stored and analyzed at the same time. All the GC analyses were made in duplicate. The experiment included four different foams and lasted for 6 weeks.

Figure 7.3 shows the results of the infinite bath experiment plotted as the average concentration of BA in foam versus time. Some scatter between samples taken at the same time is observed, which is due to the fact that the method uses a destructive approach so that a new cylinder represents each data point (after extraction and analysis). Generally the standard deviation is smaller for additional analysis of the same extract compared to additional analysis of extract from different foam samples. This is indicated by the fact that the 6 plotted points representing each analysis are usually grouped in three pairs of 2 points. This indicates that the

standard deviation is smaller for the GC-analysis compared to the standard deviation between the content of BA in different foam cylinders, which could be a combination of variation in the sizes of the foam cylinders and inhomogeneous distribution of BA in the foam panels.

Figure 7.3 shows that for all foam types most of the BA loss happens during the first 200 hours, and decreases afterwards. There is however a difference in the total quantity of BA lost by the four different foam types. This is best shown by Figure 7.4, where the total loss is shown as a percentage of the total initial BA concentration. The foam blown with CFC-11 is shown to lose approx. 17%, while the foams blown with HCFC-141b and HFC-245fa lose approx. 20%. The lowest loss is observed for foam blown with HFC-134a, which loses only 10% after almost 6 weeks.

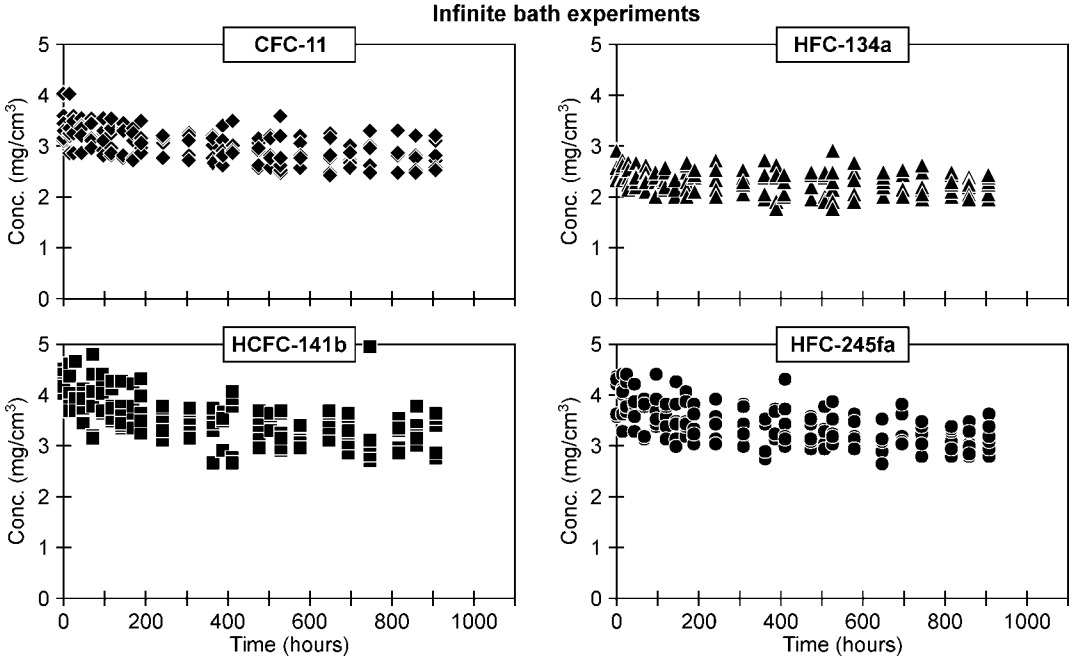


Figure 7.3. Results of the infinite bath experiment. The measured concentration of BA in foam blown with four different blowing agents versus time.

When compared to the gravimetric method experiment, where the loss observed was 8-10% for CFC-11 and HFC-245fa and 1-2% for HCFC-141b and HFC-134a after 6 weeks, this shows that the gravimetric method underestimates the total loss, and can therefore not be used. The infinite bath method was expected to show the largest BA loss, since the release happens under maximal concentration gradient (the BA concentration is zero in the volume where the release happens into). The loss from a cylindrical foam sample (diameter=1cm and height=1cm) is thus shown to be between 10% and 21% over a period of 6 weeks.

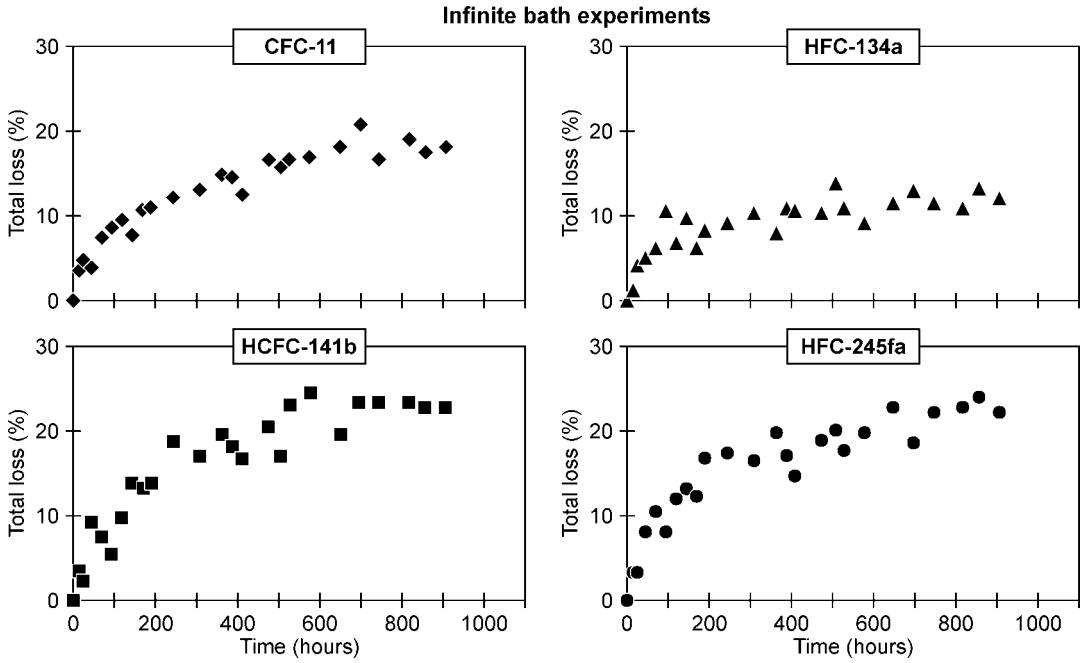


Figure 7.4 Total loss in percentage of the total initial concentration of BA for the four foam types as a function of time.

8. BATCH RELEASE EXPERIMENT

The objective of the batch release experiments is to measure the release of blowing agent from the foam. The advantages of the batch release experiments are that they are simple, cheap and easy to maintain, which implies that several experiments can be performed within the time and economical constraints of the project. Three different experiments were conducted in order to examine different factors controlling the gas release.

- Experiment 1: Examines the release from foam blown with four different blowing agents
- Experiment 2: Examines the influence of foam cylinder size on the release
- Experiment 3: Examines the release variability from foam processed by four different manufacturers (A, B, C, and D)

One disadvantage of the batch experiment is that the BA release rate might be influenced by the build-up of BA in the gas phase, which would lower the concentration gradient between the foam and air and thereby lower and underestimate the release. If pseudoequilibrium between the foam and the air is reached it will make it more difficult to interpret the results. However, this effect can be minimized by having a large air to foam volume ratio.

8.1 Experimental set-up of the batch release experiment

Foam cylinders were cut using a cork bore (1cm diameter and 1cm height for experiment 1 and 3) and placed in a 1-liter closed glass container equipped with a Teflon coated rubber septum. The foam to air volume was approx. 1444. Headspace samples were withdrawn and analyzed by gas chromatograph over time. The experiments ran for six weeks at room temperature. Control experiments (without foam but containing BA) were run in parallel.

8.2 The release of BA from foam blown with four different BAs

The objective of the experiment was to evaluate the release from foam blown with four different BAs. In addition the results will be compared with the results obtained from the flux chamber experiments and the infinite bath experiment using solvent extraction for comparing different approaches. The batch experiments were all conducted with foam obtained from supplier B.

Figure 8.1 shows the total mass loss of BA versus time - including results from a control experiment. For all foam types most of the BA loss happens during the first 150 to 200 hours, and decreases afterwards. The total loss is approx. 600 μg for CFC-11, HCFC-141b, and HFC-245fa, but is lower for HFC-134a, at approx. 250 μg. In order to compare the different foam types the loss is calculated as a percentage of the total initial BA concentration. Figure 8.2 shows the total loss in percentage of the total initial concentration of BA for the four foam types as a function of time. The foam blown with CFC-11 is shown to lose approx. 17%, while the foams blown with HCFC-141b and HFC-245fa lose approx. 20-22%. The lowest loss is observed for foam blown with HFC-134a, which loses only 10%. This experiment can however not determine whether the observed differences stem from differences between the physical/chemical properties of the BAs, or from differences between the properties of the different foam samples.

Figure 8.1 also shows the concentrations measured in the control experiment. Some variation can also be seen in the experiments with HFC-134a and HFC-245fa, probably due to the fact that the concentrations in these experiments were much higher than in the release batches. Uncertainty is increased when samples with high concentration are diluted before GC-analysis. That also explains the higher variation in the experiments with foam blown with CFC-11 and HCFC-141b, since the gas samples have been diluted during the second half of the experiment due to high concentrations obtained. The control experiment, however, shows no indication of continuos BA losses through needle holes in the septa or by sorption to the septa material.

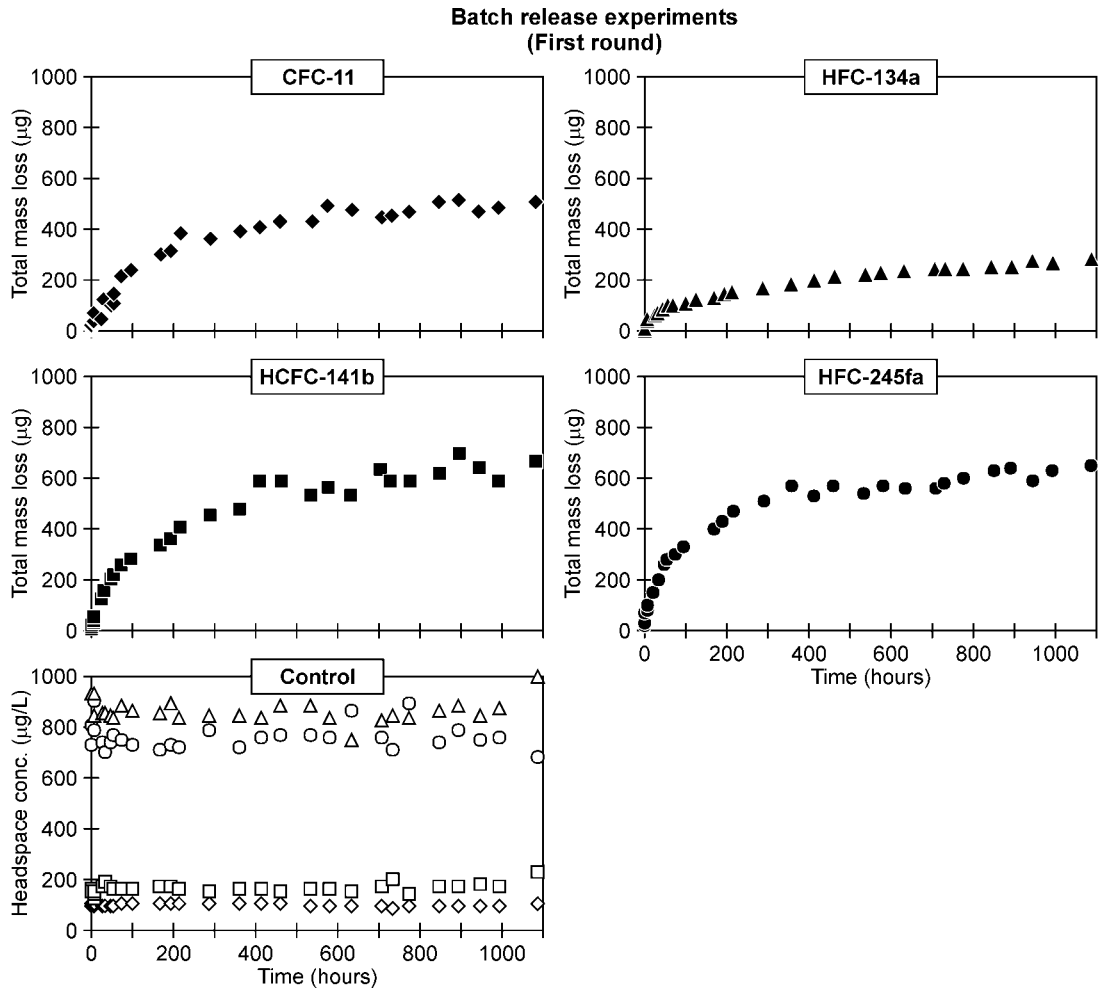


Figure 8.1. Total mass loss of BA from foam blown with four different BA versus time. Control experiment: ◆: CFC-11, ▲: HFC-134a, ■: HCFC-141b, and ●: HFC-245fa.

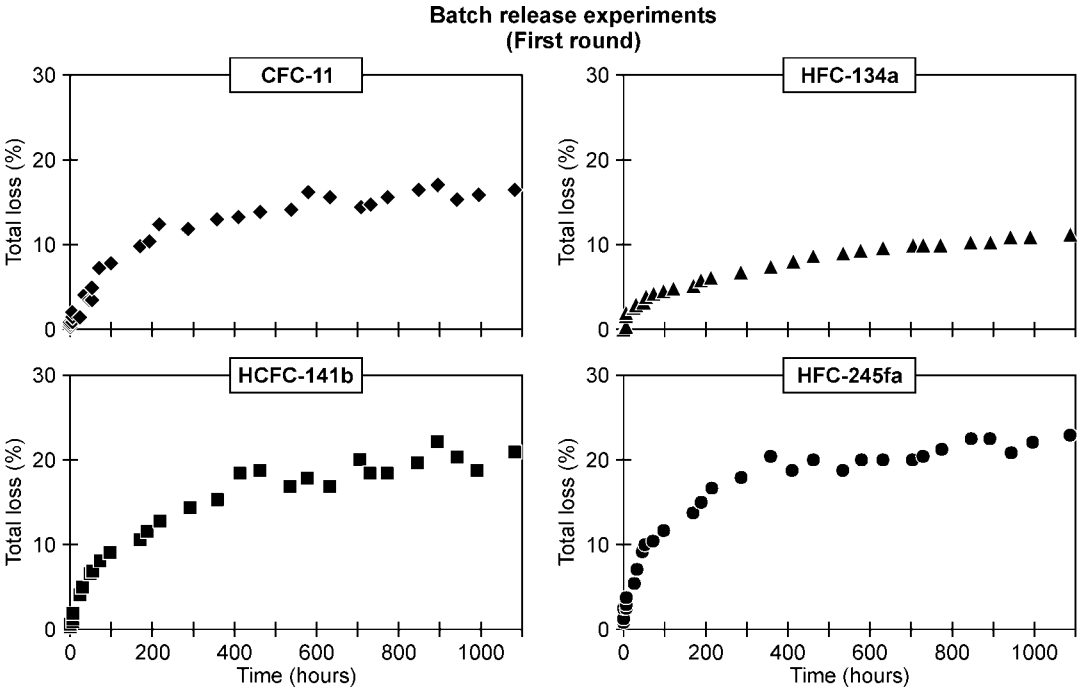


Figure 8.2. Total loss of BA in percentage from foam blown with four different BA versus time.

In order to examine whether the release decrease might be due to equilibrium between the gas and the foam the containers were opened, emptied of gas and closed again. The gradient between the gas phase and the foam is reduced when the gas concentration increases, which may lead to a reduced diffusion rate. The results are available in the Appendix 6, and show that the release continues with approximately the same speed after the containers are emptied. Calculating the slopes of the release curves best illustrates this (see table in Appendix 6). The reduction in release speed after 200 hours cannot therefore be attributed to a blocked diffusion due to equilibrium between the gas phase and the foam. Based on these observations we can conclude that the measured BA loss of 10-21% is not underestimated.

8.3 The release of BA from foam particles with different sizes

The objective of the experiment was to evaluate if the release of BA is controlled by the size of the foam particle. Nine batch experiments were carried out each containing one cylinder-shaped foam sample. The batch experiments were all conducted with foam blown with HCFC-141b obtained from supplier B.

Figure 8.3 shows the total loss in percentage of the content of BA in the foam samples. Each figure describes one experiment and the volume of the foam sample is shown in the top of the figure. The figures show that the largest loss is obtained from the smallest foam particle: in the experiment with a 0.8 cm^3 particle the loss is 19% of BA, while it is only 3% for a 12.8 cm^3 particle. The loss appears to increase significantly when the particle is smaller than 2.2 cm^3. This experiment is coherent with the batch release experiment for HCFC-141b, which was performed with a foam cylinder of 0.8 cm^3 and showed a loss of 18% after 1000 hours (cf. section 7.2).

Table 8.1 shows an overview of the experiments carried out and the BA losses measured. Figure 8.4 shows an inverse correlation between the measured BA loss in percentage of the total initial content and the diameter of the foam particle to the second order. This is equivalent with a proportional relation of the mass released, M (in μg) to the surface area in combination with an inverse relation to the particle diameter, which indicates the following simple relationship (assuming a spherical geometry):

$$M = F \cdot t = A \cdot D \cdot \frac{C_{tot}}{r} \cdot t = 4\pi r^2 D \cdot \frac{C_{tot}}{r} \cdot t$$

where F is the flux (μg/h), t is time (h), A is particle surface area (cm^2), D is effective diffusion coefficient (cm^2/h), C_{tot} is total BA concentration (μg/cm^3), and r is radius (cm).

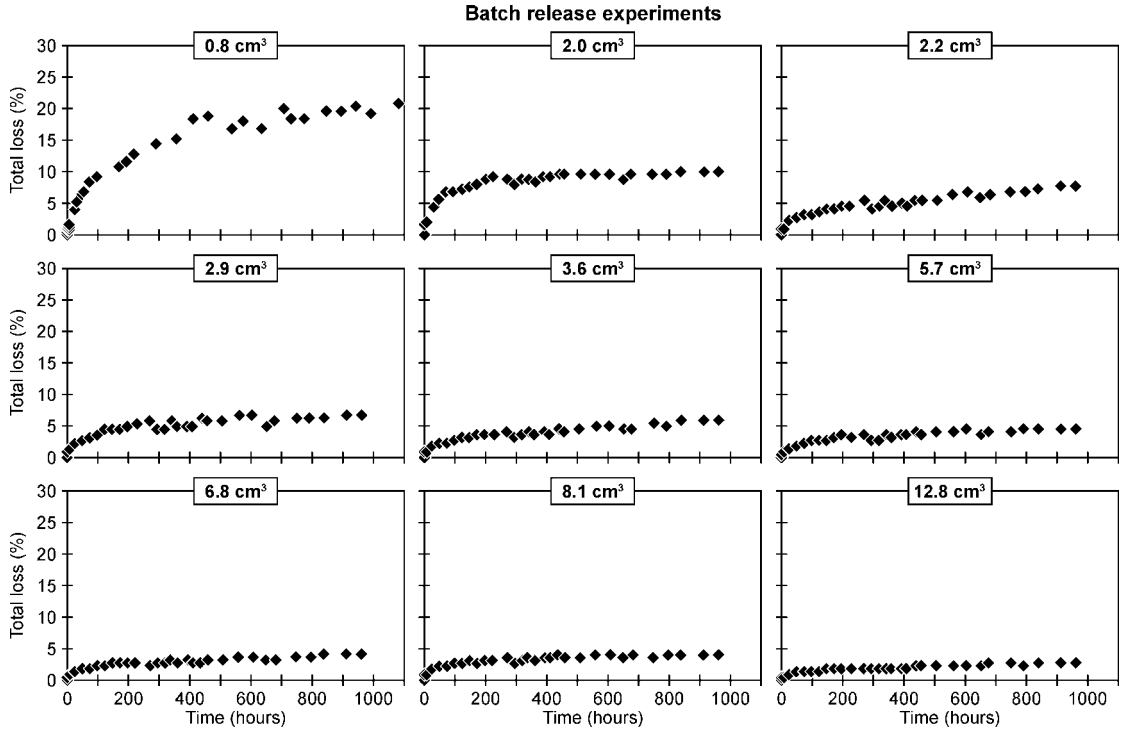


Figure 8.3. The total loss of HCFC-141b in percentage from foam particles with different sizes versus time.

Table 8.1. The summarized results from batch release experiments containing foam blown with HCFC-141b. The proportions of the foam cylinders and the obtained losses are listed in the table.

Batch	Diameter	Height	Volume	Surface area	Total mass loss	Total loss
	cm	cm	cm^3	cm^2	µg	%
1	1.00	1.00	0.8	4.7	523	19
2	1.29	1.52	2.0	8.8	756	10.2
3	1.4	1.42	2.2	9.3	621	7.6
4	1.54	1.58	2.9	11.4	697	6.8
5	1.65	1.69	3.6	13.0	762	6
6	1.90	2.02	5.7	17.7	975	4.6
7	2.05	2.06	6.8	19.9	992	4.1
8	2.16	2.22	8.1	22.4	1151	4
9	2.50	2.60	12.8	30.2	1328	2.8

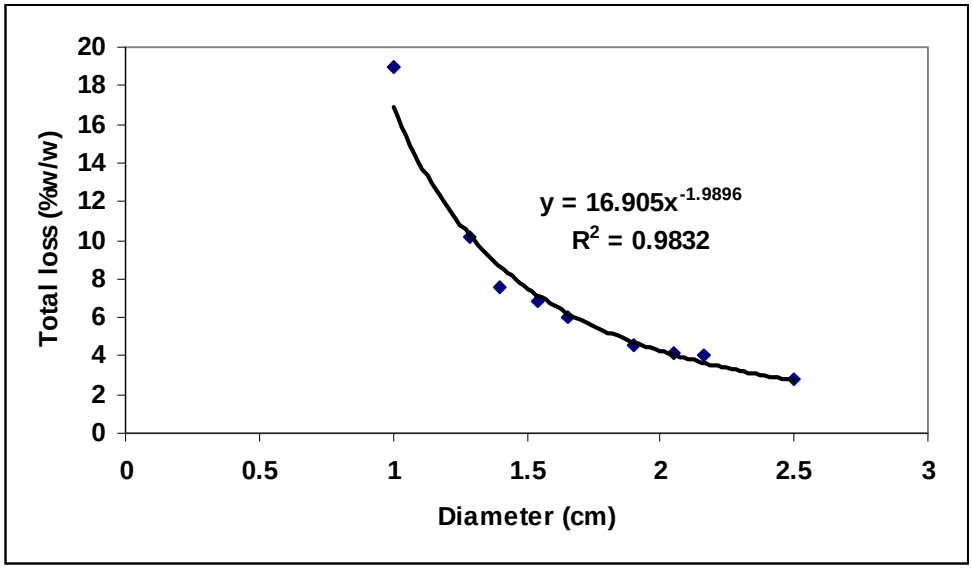


Figure 8.4. Correlation between the measured total BA loss and the diameter of the foam cylinders

8.4 The release of BA from foam produced by four different manufacturers.

The objective of the experiment was to evaluate the release variability between foam products. The experiment was carried with foam containing HFC-245fa produced by four different manufacturers. Table 8.2 shows the total amount of BA in the four foam panels. For details about foam analyses see section 4.3.

Table 8.2. Total amount of HFC-245fa in foam panels from four different suppliers

Parameter	Unit	Supplier			
		A	B	C	D
Density, ρ_{foam}	g/L	37.4	30.4	30.5	30.3
Total content of blowing agent in foam	g/L	2.84	3.68	4.20	5.63
	% w/w	7.62	11.75	13.74	18.23

Figure 8.5a shows the total mass loss as a function of time while figure 8.5b shows the total loss in percentage of the total content of BA. The measured concentration from a control batch is also shown in Figure 8.5a. There appears to be a quite significant difference between the losses of HFC-245fa from the four different samples. The smallest loss observed, about 5.5%, is from foam produced by manufacturer A, with foam from manufacturers C and D showing only slightly higher losses of 8.1% and 7.5% respectively. However, foam produced by manufacturer B showed a much higher loss of 24%. The experiment is also coherent with another experiment conducted with HFC-245fa-blown foam from the producer B (same panel), where a total BA loss of 22% was observed after 850 hours (cf. section 7.2). This experiment shows that the BA loss can vary a lot depending on the PUR product, and that the properties of the foam have a significant influence on the release of BA. It also shows that the panel from manufacturer B blown with HFC-245fa is not representative of panels blown with HFC-245fa. Based on these results including the total contents given in table 8.2 the panel from manufacturer C and D seems more representative. This is further studied by use of flux chamber experiments as described in section 9.4.

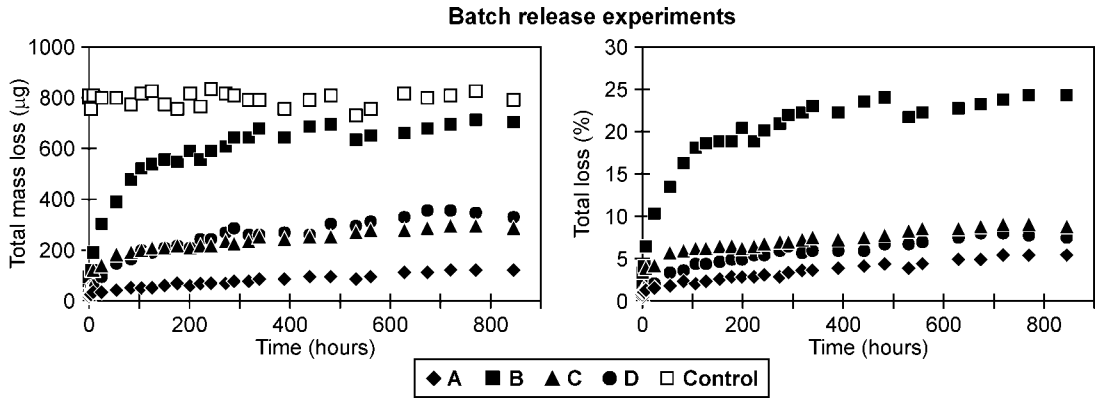


Figure 8.5. a. Total mass loss of HFC-245fa from PUR foam produced by four manufactures versus time. b. Total loss of HFC-245fa in percentage from PUR foam produced by four manufactures versus time.

9. FLUX CHAMBER RELEASE EXPERIMENTS

The objective of the experiment was to determine the amount of blowing agent released upon shredding as a function of time up to six weeks. The objective was met by carrying out flux chamber release experiments. The advantages of the flux chambers are that the atmosphere in the chamber can be controlled and that a mass build-up is avoided. However, the flux chambers are technically more complex and time consuming, which limits the number of experiments. Two different experiments were conducted.

- Experiment 1: Examines the release from foam blown with four different blowing agents
- Experiment 2: Examines the release variability from foam processed by different manufactures (B, C, and D)

Besides a control experiment to verify the experimental method was carried out. The result of the control experiment is given in section 9.2, while the results for CFC-11 and HCFC-141b is given in section 9.3. The results for HFC-134a and HFC-245fa, where releases from foams produced by different producers were investigated are given in section 9.4.

9.1 Experimental set-up of the flux chamber

The test chamber consists of a stainless steel cylinder, 25-cm long by 15-cm i.d. The steel cylinder is closed at one end and equipped with a steel lid fitted with rubber O-rings to ensure a gas-tight fit. The lid contains an inlet port for gas. An outlet port is positioned at the bottom-end of the cylinder. A perforated screen is located 8 cm above the bottom of the cylinder to place the foam cubes. A sampling port is located at the bottom of the cylinder to enable taking gas samples with a syringe needle. The sample port is equipped with teflon coated silicone septum. Both in- and outlet are equipped with a valve, which enables closing the container when changing the gas, (dis)-connecting other chambers.

The nitrogen (>99.999%) gas flask, which feeds the test chamber, is equipped with a special reduction valve in order to obtain a very low pressure. The pressure was 0.03 bar. In order to calculate the exact gas amount released from the foam, the flow must be kept constant. A gas tight piston pump (FMI Lab Pump, model QG, Fluid Metering Inc.) controls the flow through the system. The gas outflow can be measured by a bubble flow meter. The inlet flow was 12 mL/min resulting in a retention time of 6.2 hours. The chamber experiment was carried out at room temperature. Gas samples were taken directly from the outlet of the chambers through a sampling port equipped with a septum. Pictures of the flux chamber set up are inserted in Appendix 7.

In total five flux chambers were run in parallel: four chambers with foam and one control chamber. The four chambers contained four foam types blown with four different blowing agents. The foam was cut into a number of small cylinders using a cork bore (diameter=1cm; height=1cm) and placed in the chamber. The number of foam cylinders placed in each chamber was determined by the sensibility on the GC – so that fewer foam cylinders were needed to get a measurable concentration for CFC-11 in comparison with HFC-134a. The chamber was closed and the first gas sample was taken after 15 min.

To validate the flux chamber method a control experiment was carried out. The control flux chamber contained a known amount of liquid HCFC-141b in small glass container equipped with a needle. Before start up and at the end of the experiment the liquid sample was weighed. The mass loss of HCFC-141b from the container was measured over the full experiment time by analysing gas samples taken in the outlet.

9.2 Results from the control experiment

In the control experiment it was found that a total mass of 2.0664g determined by weight had been lost from the liquid source of HCFC-141b. This mass loss was compared with the measured accumulated mass loss based on outlet concentration and flow measurements. Figure 9.1a shows the measured outlet concentrations versus time. During the first 24 hours the outlet concentration increased until a steady state level is reached at approx. 3000 µg/L. A constant release over time should give a linear curve for the accumulated total mass loss of HCFC-141b, which also is the case - shown in Figure 9.1b. After 1100 hours the accumulated mass loss is 2.1074g which is only 2% more than the 2.0664g. The control experiment therefore shows that there are no losses in the experimental set up.

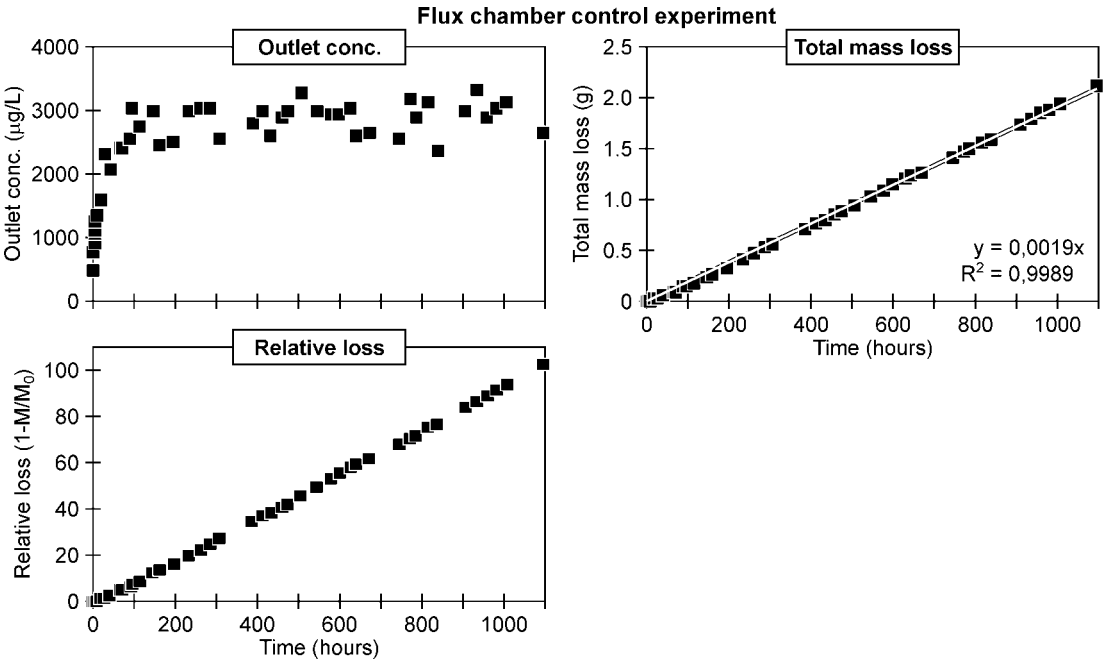


Figure 9.1. Results from a control experiment conducted with HCFC-141b. a. Measured outlet concentrations versus time. b. Accumulated mass loss of HCFC-141b versus time. c. The relative loss in percentage.

9.3 Results from the flux chamber experiments conducted with foam blown with CFC-11 and HCFC-141b

Figure 9.2 shows the total mass loss as a function of time for CFC-11. The figure also shows the total loss in percentage of the total initial concentration of BA. Figure 9.3 shows similar results for HCFC-141b. Both experiments were made with foam panels provided from

supplier B. The total mass loss is calculated using the measured outlet concentration and flow. In order to compare the results, the outlet concentrations have been divided by the number of foam cylinders in each flux chamber, so the figures show the accumulated total mass loss from one foam cylinder. The figures all show the same trend: most of the BA loss happens during the first 150 to 200 hours, and decreases afterwards and from 400 hours the release is almost linear. After 1100 hours the total loss sums up to approx. 600 µg for CFC-11, and a little higher for HCFC-141b. The foam blown with CFC-11 is shown to lose approx. 20%, while the foams blown with HCFC-141b looses 28%.

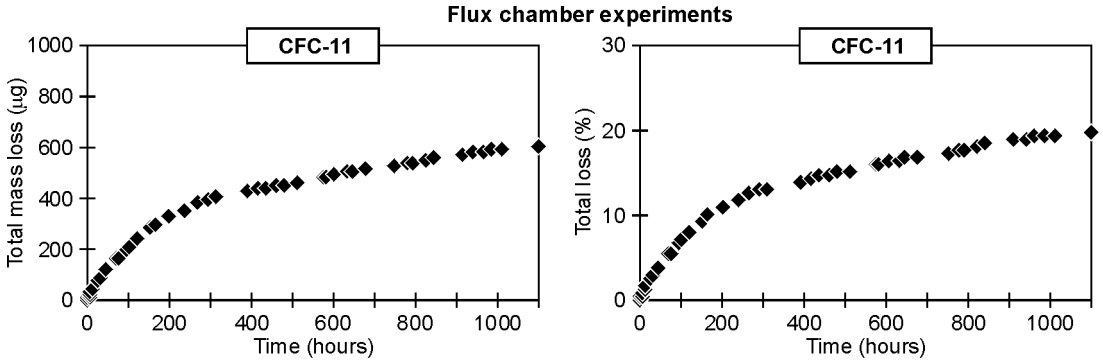


Figure 9.2. Accumulated total mass loss of BA from foam blown with CFC-11 given in absolute mass and as percentage of the initial total content of BA.

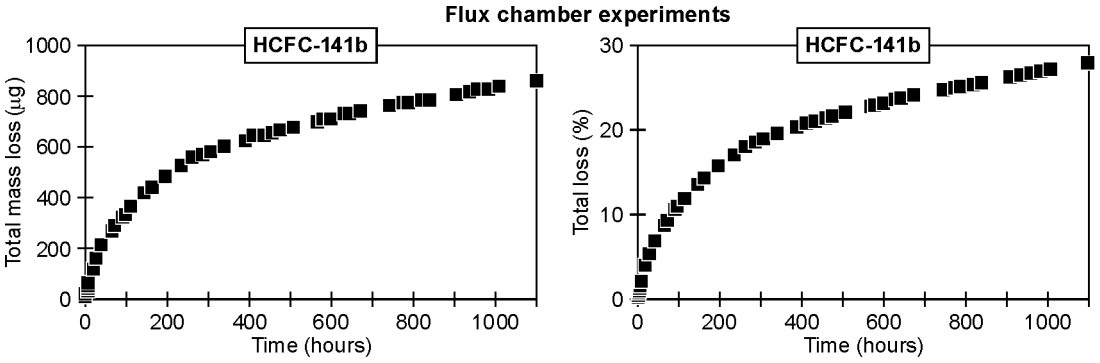


Figure 9.3. Accumulated total mass loss of BA from foam blown with HCFC-141b given in absolute mass and as percentage of the initial total content of BA.

9.4 Results from the flux chamber experiments conducted with foam blown with HFC-134a and HFC-245fa

Batch release experiments showed a quite significant difference between losses of HFC-245fa from foam produced by four different manufactures. Therefore flux chamber experiments using foams produced by different users for both HFC-134a and HFC-245fa were used. HFC-134a and HFC-245fa were chosen due the expected increase in use in the future. In addition, the experiment with HFC-245fa produced by manufacturer B was conducted twice to investigate the reproducibility of the flux chamber approach. Table 9.1 shows the total amount of HFC-245fa and HFC-134a in foam panels from three different suppliers.

Table 9.1. Total amount of HFC-245fa and HFC-134a in foam panels from three different suppliers

Parameter	Unit	Supplier		
		B	C	D
HFC-245fa				
Density, ρ_{foam}	g/L	30.4	30.5	30.3
Total content of blowing agent in foam	g/L	3.68	4.20	5.63
	% w/w	11.75	13.74	18.23
HFC-134a				
Density, ρ_{foam}	g/L	39.0	38.6	33.7
Total content of blowing agent in foam	g/L	2.78	3.32	2.52
	% w/w	7.03	8.61	7.48

Figure 9.4a shows the total mass loss of HFC-245fa as a function of time while figure 9.4b shows the total loss in percentage of the total content of BA. In correspondence with the conducted batch experiments (cf. section 8.4) there appears to be a quite significant difference between the losses of HFC-245fa from the three different samples. The smallest losses observed are from foam produced by manufacturers C and D, showing a rather similar loss of 7.6% and 9.5% respectively. However, foam produced by manufacturer B showed a much higher loss of 28-30%. Despite the fact that the experiment B-x showed a slightly lower total loss of 25%, a rather nice correspondence is observed between the duplicate experiments B and B-x, especially within the first 500 hours. The flux experiment is also coherent with batch experiments conducted with HFC-245fa-blown foam from four different producers (cf. section 8.4), where HFC-245fa blown foam from manufacturers C and D showed losses of 8.1% and 7.5% respectively, while foam produced by manufacturer B showed a loss of 24% after 850 hours. The foam from supplier C and D with releases of about 8% thus seems to be more typical.

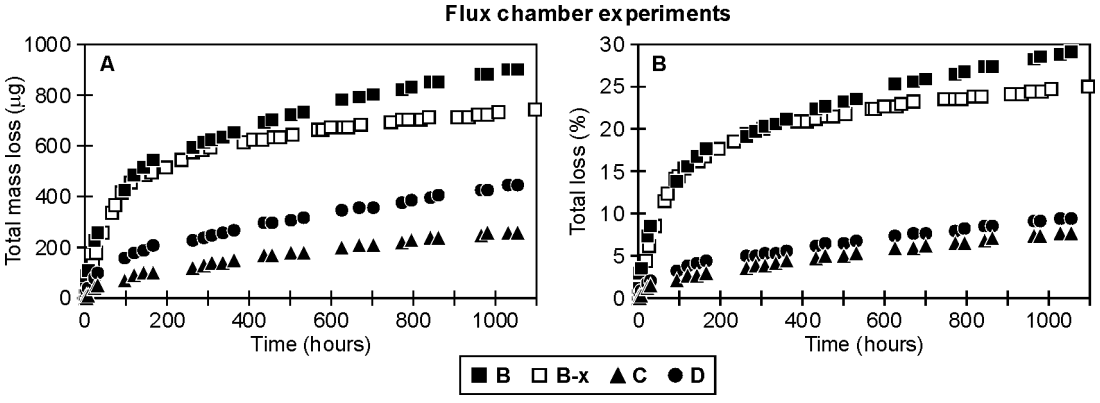


Figure 9.4. a. Total mass loss of HFC-245fa from PUR foam produced by three manufactures (B, C, and D) versus time. b. Total loss of HFC-245fa in percentage from PUR foam produced by three manufactures.

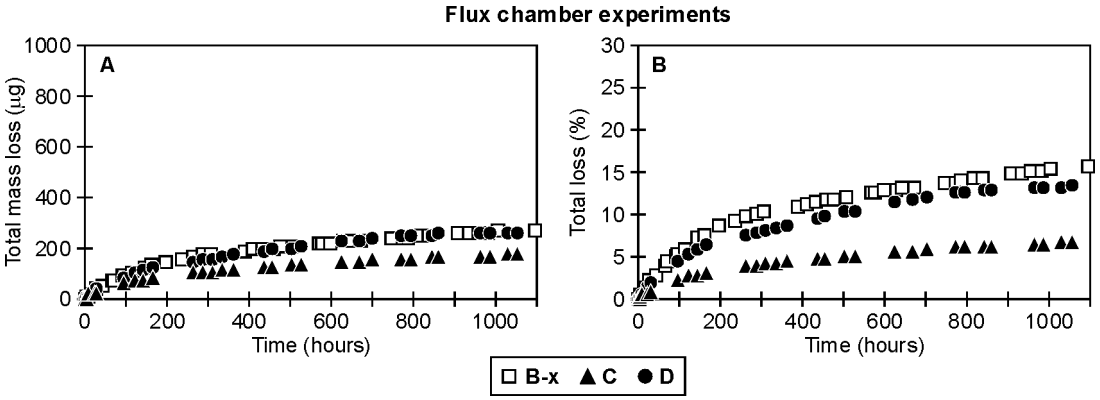


Figure 9.5. a. Total mass loss of HFC-134a from PUR foam produced by three manufactures versus time. b. Total loss of HFC-134a in percentage from PUR foam produced by three manufactures (B, C, and D) versus time.

Figure 9.5a shows the total mass loss of HFC-134a as a function of time while figure 9.5b shows the total loss in percentage of the total content of BA. The smallest loss, about 7%, was observed from foam produced by manufacturer C. Foam produced by manufacturers B and D showed much higher but very similar losses of 15% and 13% respectively.

This experiment shows that the BA loss can vary a lot depending on the PUR product, and that the properties of the foam have a significant influence on the release of BA. Since the panel blown with HFC-245fa from manufacturer B gave a much higher loss compared to the panels from the other suppliers it is questionable whether manufacturer B is representative of panels blown with HFC-245fa in general. Based on the results from both the conducted batch and flux chamber experiments, the panels from manufacturer C and D seem more representative. The same cannot be concluded for the experiment conducted with HFC-134a. The highest loss (15%) of HFC-134a is observed using foam from supplier B, but this is only slightly higher than the loss of 13% in experiment with foam from supplier D. The panels from manufacturers B and D seem more representative compared to manufacturer C, which shows a loss of only half the amount. This experiment shows that it cannot generally be concluded that panels from manufacture B overestimates the losses or is not representative. However, if the test panels truly represent the insulation foam used in freezer/refrigerators in the market this study shows the loss of BA will vary between products.

9.5 Model simulation

9.5.1 Evaluation of flux chamber experiments by the double compartment model

The double compartment model has been used for simulating the flux chamber experiment for the four different blowing agents. Figure 9.6 shows the mass release as a function of square root to the time for one of the flux chambers with HFC-245fa-blown foam. The fitted and calculated parameters for the four different experiment can be seen in Table 9.2. The magnitude of the diffusion coefficient for the short-term and long-term releases are close to the observed values in the first study carried out at Environment & Resources DTU[8]. Three out of four long-term diffusion coefficients are very close to each other. The diffusion coefficient for HCFC-141b is about 50% larger. Others have also found larger diffusion coefficients for foams blown with HCFC-141b[14]. In general the magnitudes of the determined long-term diffusion coefficients are close to the calculated values based on Hong and co-workers studies as given in Table 4.1.

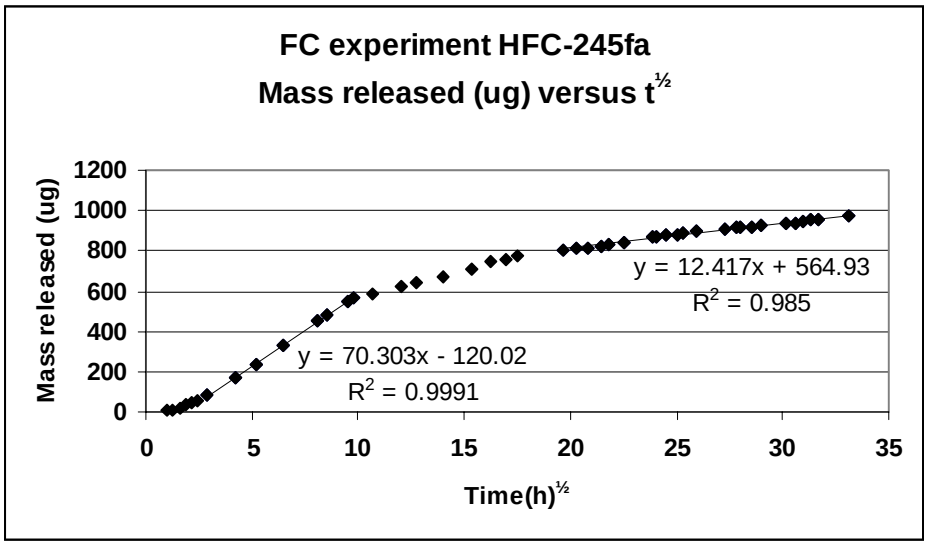


Figure 9.6. Mass released (in μg) as a function of the square root of time for flux chamber experiment using foam blown with HFC-245fa. The fitted lines for the short-term release and the long-term release are shown with the slope and the correlation coefficient (R^2).

Figure 9.7 and 9.8 show comparisons of the simulated and the measured data for the accumulated mass release and the flux, respectively. There is a good agreement between the simulated and the measured data. Figure 9.9 shows a similar graph for the experiment with foam blown with CFC-11. The graph shows that in this case the initial measured fluxes are much lower that the simulated fluxes. This might be due to loss of a portion of the blowing agent before the experiment was started. However this has no effect on the simulated long-term fluxes and the extrapolation of the flux chamber experiments to the future period (from times over 6 weeks). For all four foams about 10-15% of the total BA mass was contained in the broken cell fraction, leaving the rest in the closed cell fraction.

Table 9.2. Parameters in the double compartment model using the four blowing agents. All experiments used cylinders with d=1cm and h=1cm.

BA	Short-term release				Long-term release			
	$M_{0,1}$[a] (μg)	α_1[b] (μg $t^{-½}$)	R^2[c]	D_1[d] ($10^{-12}m^2s^{-1}$)	$M_{0,2}$ (μg)	α_2 (μg $t^{-½}$)	R^2	D_1 ($10^{-14}m^2s^{-1}$)
CFC-11	350	28.8	.997	4.1	2340	13.8	.998	2.1
HFC-134a	305	15.3	.997	1.5	1890	11.0	.999	2.1
HCFC-141b	370	37.3	.999	6.0	2500	17.2	.999	2.9
HFC-245fa	632	70.3	.999	7.5	2240	12.4	.985	1.9

a: $M_{0,1}$ used as fitting parameter

b: Slope of best fitting line to M_t versus $t^{½}$

c: Correlation coefficient for the line fit

d: Calculated diffusion coefficient from expression $D = \frac{\pi \cdot \alpha^2}{4M_0^2 \cdot (A/V)^2}$ given from equation 6

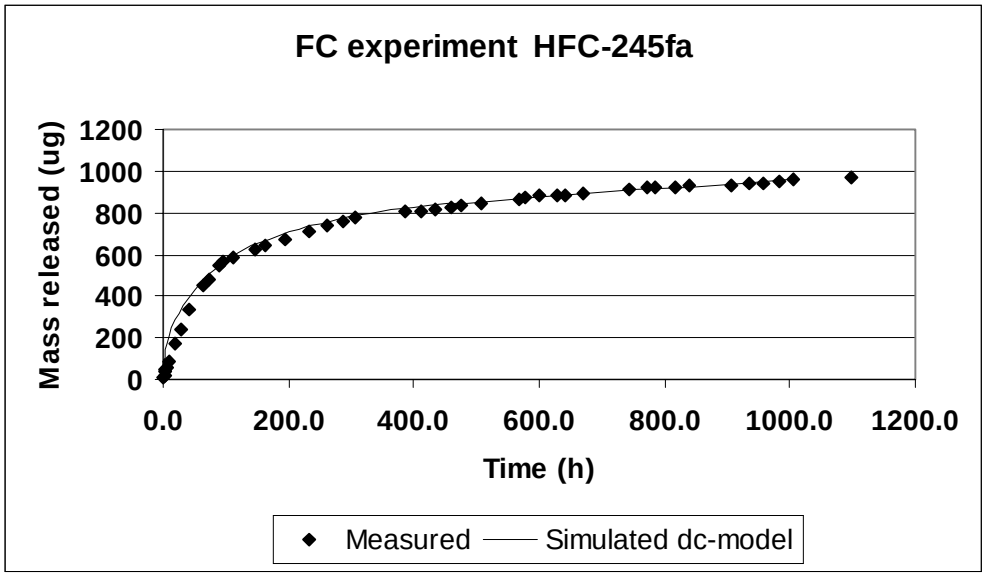


Figure 9.7. Measured and simulated (using the double compartment model) mass release in flux chamber with foam blown with HFC-245fa.

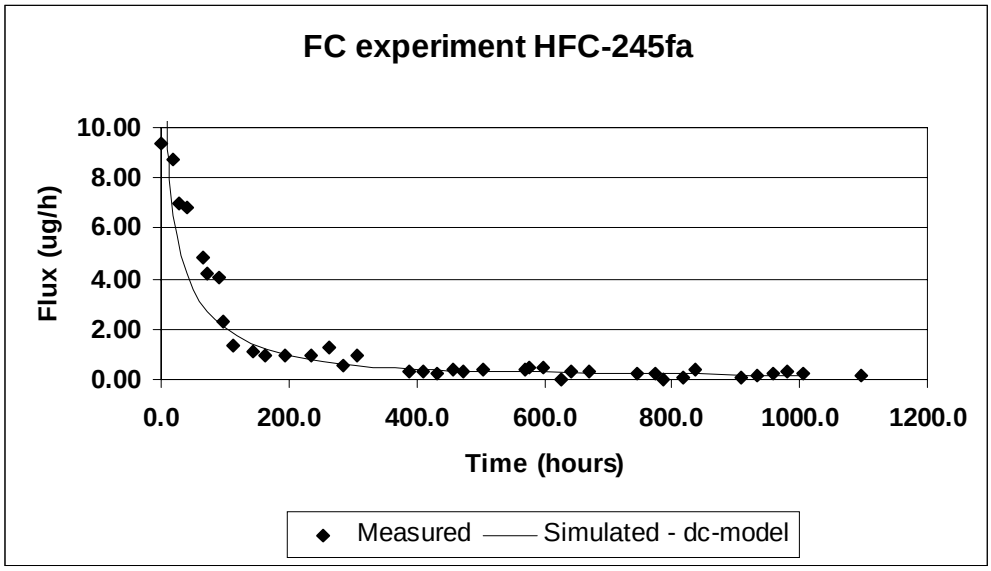


Figure 9.8. Measured and simulated (using the double compartment model) fluxes in flux chamber with foam blown with HFC-245fa.

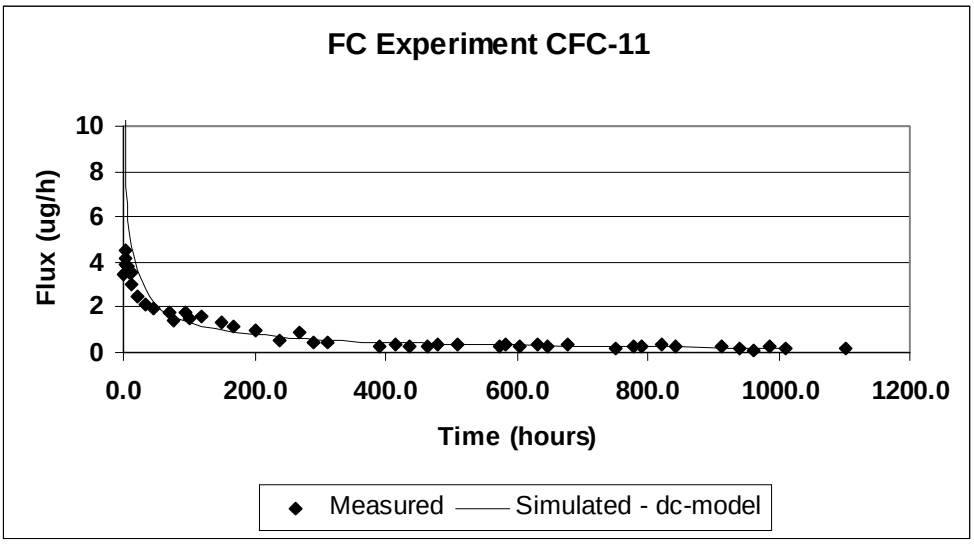


Figure 9.9. Measured and simulated (using the double compartment model) fluxes in flux chamber with foam blown with CFC-11.

9.5.2 Extrapolation of flux chamber results to long-term releases

Using the model for releases from cylindrical shapes under infinite bath conditions (equation 3 and 5 in section 4.2.) the fraction of the initial mass released for different times can be calculated for different blowing agents (using the estimated long-term diffusion coefficients given in Table 9.2). The average sizes in the different size distribution categories (confer section 6.2 for details) has been used in the calculations. The model simulations are presented in Figure 9.10-9.13 for the four different blowing agents. The model assumes that the released BA will be transported out of the system, in a landfill equivalent to an escape of BA either by the gas emitted from the landfill or by degradation in the landfill environment.

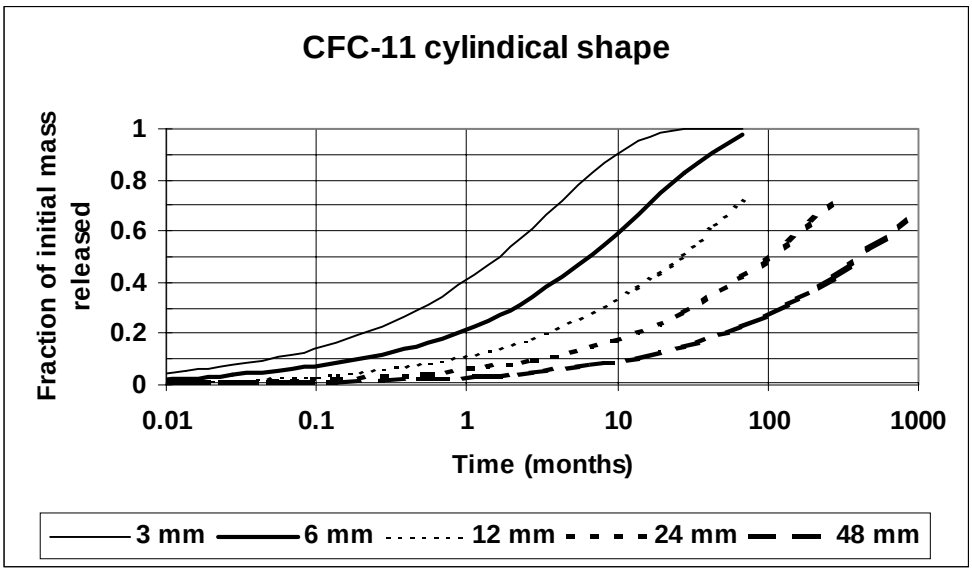


Figure 9.10. The fraction of initial mass released as a function of time and particle size for CFC-11.

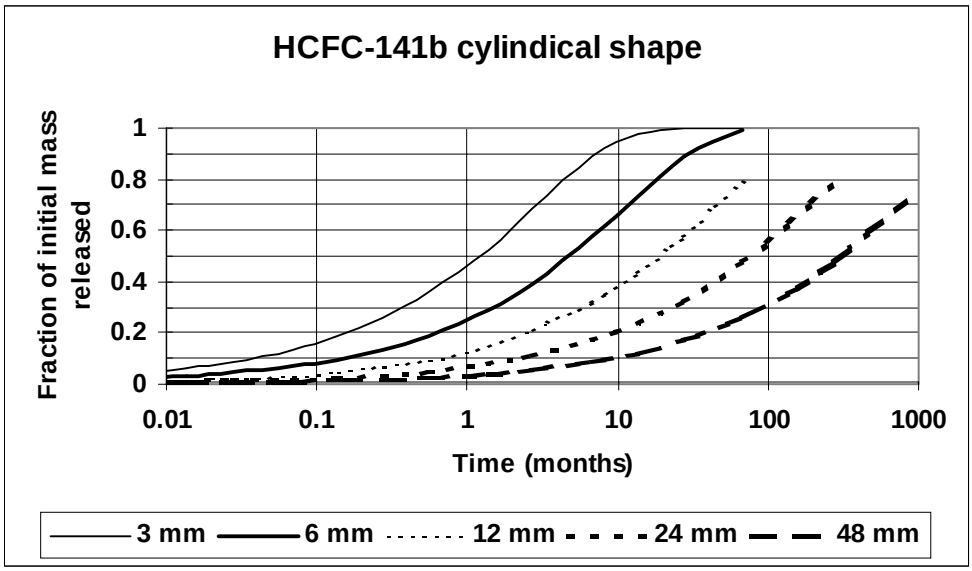


Figure 9.11. The fraction of initial mass released as a function of time and particle size for HCFC-141b.

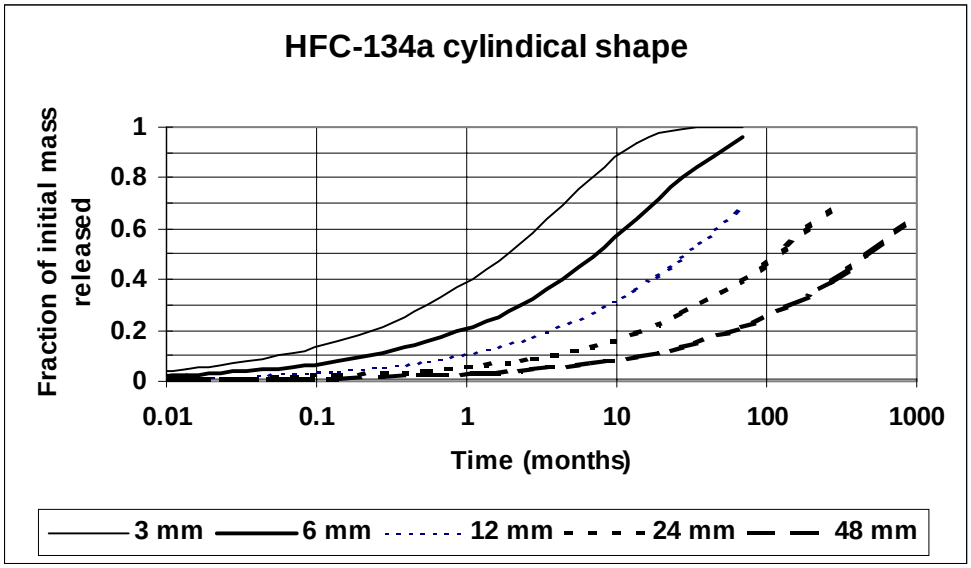


Figure 9.12. The fraction of initial mass released as a function of time and particle size for HFC-134a.

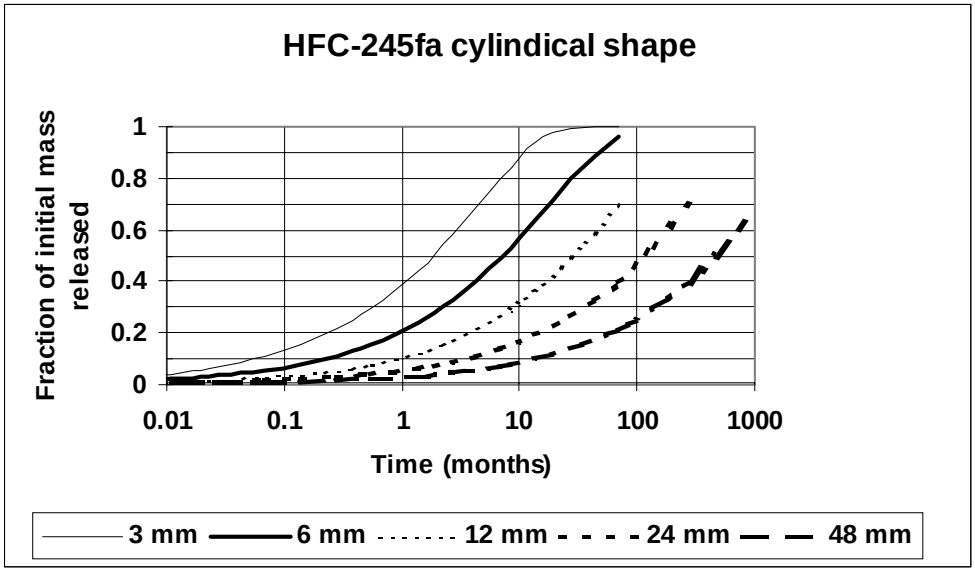


Figure 9.13. The fraction of initial mass released as a function of time and particle size for HFC-245fa.

Due to the relatively small differences in diffusion coefficients determined, the curves are quite similar. As an example of reading the curves, figure 9.10 shows that after 10 months 60% of the initial content (in the closed cell fraction) has been released from a 6mm diameter by 6mm height cylinder. This assumes that the particle keeps its diffusional properties after product decommissioning and disposal of foam in landfill.

10. INSTANTANEOUS RELEASE EXPERIMENT

To quantify the instantaneous release during shredding due to breakage of closed cells a larger experimental set-up was used, where foam was shredded in a closed environment. Foam blown with three types of blowing agents (CFC-11, HCFC-141b, and HFC-245fa) was included in the experiment. Foam blown with HFC-134a was not included due to the high analytic detection limit, which would require that a disproportionately large foam sample should be shredded in the glove box.

In addition it was examined if the release is related to the particle size of the shredded foam. Experiments were carried out with foam blown with CFC-11 where the foam was shredded into four different size fractions. Table 10.1 shows the glove box experiments conducted. At the end of the experiment three different size fractions of the shredded material were collected and placed in a flux chamber in order to determine the release from the shredded material during the following six weeks. The flux chamber experiment using shredded material is described in section 10.1.

10.1 Experimental set-up of instantaneous release experiment

A defined foam sample was hand-sectioned, simulating real shredding, in a closed container and the loss determined by taking gas samples every 1-2 minutes followed by gas chromatographic analysis. The release experiments were conducted in a glove box, which normally is used for anaerobic experiments. The glove box is made of thick transparent polyvinyl chloride membrane and has a total volume of 1335 litres. Pairs of gloves are inserted through the walls (hence the name of the box), which makes it possible to work inside the glove box from the outside. The glove box has as standard equipment of two ventilators, which should ensure that the gas phase in the glove box always is fully mixed. In addition a fan was also placed in the box. A photo of the glove box is in Appendix 8.

A bigger foam sample was cut out of the test panels and placed in the glove box. The glove box was then closed and the shredding started. The shredding of the foam was generally carried out by a combination of cutting using a knife and breaking by hand. To obtain smaller size fractions a grater and a food blender were used (cf. Table 10.1). Based on analysis of the size distribution of real shredded foam and on the look of the artificially shredded foam it is believed that it simulates real shredded material very well. For photos of the artificially shredded foam refer to Appendix 9. In general the whole shredding process took around 4-6 minutes. However, an exception was made in the case where a blender was used: here the foam was blended for one minute before the blender was opened.

After the first 15 minutes in the glove box the shredded foam was placed in a closed container situated inside the glove box in order to cut off emissions that were not due to the instantaneous release. After 30 minutes the experiment was terminated (glove box opened). To flush the glove box before start-up it was vacuumed and opened three times and then left open and ventilated for 2 hours. To assure that the box was empty of blowing agent a zero sample was always taken before starting shredding the foam. After the experiment the size distribution of the shredded foam was determined by sieving using standard soil sieves. Table 10.1 shows the size of the shredded foam where the main fraction is. Table 10.1 also shows how much of the total foam sample lies in the main fraction by weight.

Table 10.1: The conducted glove box experiments

Experiment	Size	Main fraction	Proportion in main fraction	Total initial weight of the foam sample	Tool used for shredding
		mm	%	g	
Blowing agent					
CFC-11	X-large	16 - 32	83.8	13.59	Knife and hand
HCFC-141b	X-large	16 - 32	73.9	16.16	Knife and hand
HFC-245fa	X-large	16 - 32	74.2	15.25	Knife and hand
Size fraction					
CFC-11	X-large	16 - 32	83.8	13.59	Knife and hand
CFC-11	Large	8 - 16	83.4	3.23	Knife and hand
CFC-11	Medium	4 - 8	77.1	3.24	Grater
CFC-11	Small	2 - 4	64.9	1.79	Food blender

10.2 Results from the instantaneous release experiment

10.2.1 Instantaneous loss from foam blown with different blowing agents

Figure 10.1 shows the instantaneous loss of BA in percentage of the total BA content as a function of time from foam blown with three different blowing agents. The calculation of the total loss is based on the measured gas concentrations, the total volume of the glove box, and the total content of BA in the foam.

The experiments show the same trend in the release of BA from the three different foams. The graphs in Figure 10.1 show that BA is released instantaneously at the shredding of the foam and continues for 6 to 7 minutes, which corresponds to the time is takes to shred all the foam. The release decreases thereafter rather rapidly and after 12 minutes no further release is observed. Fifteen minutes after start up the shredded foam is collected and placed in a closed container inside the box.

In the experiment with foam blown with CFC-11 6 gas samples were taken in different places in the glove box (incl. corners) in order to check if the glove box was fully mixed. The samples were taken 21 minutes after start up and as can be seen from Figure 10.1. The gas samples showed very similar results (standard deviation of 5%), indicating that the box was fully mixed.

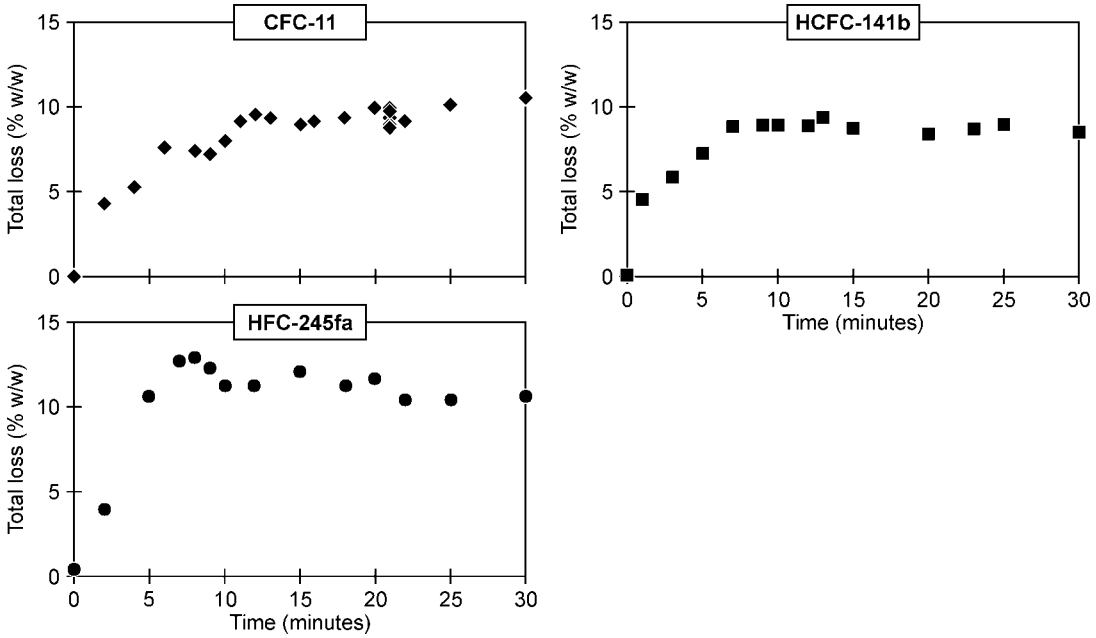


Figure 10.1. The instantaneous release in percentage during shredding of foam blown with different blowing agents within the first 15 minutes.

Table 10.2. The instantaneous release during shredding from foam blown with different blowing agents

Blowing agent	**Size**	**Main fraction mm**	**Total content of BA % w/w**	**Total loss % w/w**
CFC-11	X-large	16 to 32	13.30	9.4
HCFC-141b	X-large	16 to 32	11.62	8.8
HFC-245fa	X-large	16 to 32	11.62	11.1

The results obtained in the experiment are summarized in Table 10.2. The total loss is calculated using an average of the measured gas concentrations from 10 to 30 minutes. The experiment shows very similar results for the three foams. The instantaneous release during shredding varies very little between the different foams: from 9.4% to 11.1 % w/w when foam is shredded into foam particles of 16 to 32 mm. The instantaneous loss during shredding seems independent of the type of BA, indicating that the release is a result of the volume of open cells from the shredding process rather than the type of BA. This experiment shows an average loss of 10% w/w of BA instantaneously when foam is shredded to particles of 16 to 32 mm.

10.2.2 Instantaneous loss from foam blown with CFC-11 shredded into different sizes

Figure 10.2 shows the loss of BA in percentage of the total initial content from foam blown with CFC-11 shredded into four different sizes as a function of time.

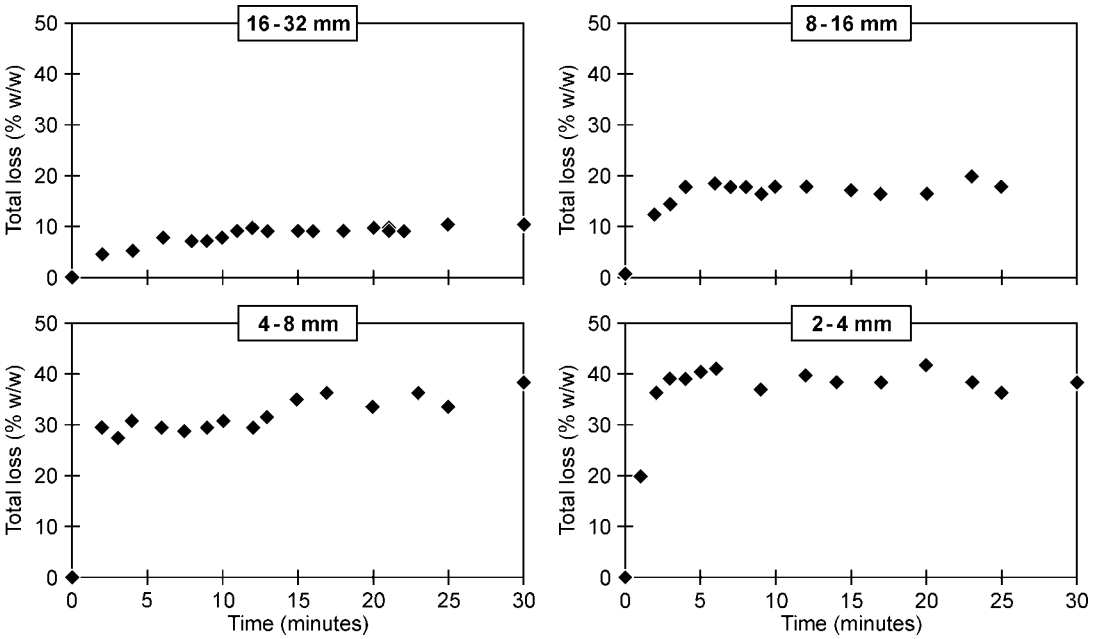


Figure 10.2. The instantaneous release in percentage during shredding of foam blown with CFC-11 shredded into four different sizes within the first 15 minutes.

Figure 10.2 shows that the BA is released instantaneously when the shredding of the foam starts and is coherent with the observations from the first glove box experiment. The total loss is calculated using an average of the measured gas concentrations from 10 to 30 minutes. The results are summarized in Table 10.3.

Table 10.3. Loss from foam blown with CFC-11 shredded into four different size fractions

Blowing agent	**Size**	**Main fraction**	**Total content of BA**	**Total loss**
		mm	**% w/w**	**% w/w**
CFC-11	Small	2 to 4	13.30	38.7
CFC-11	Medium	4 to 8	13.30	33.8
CFC-11	Large	8 to 16	13.30	17.6
CFC-11	X-large	16 to 32	13.30	9.4

This experiment shows that the instantaneous release of BA is controlled by the particle size of the shredded material. The loss of BA varies between 10% to 40% when foam is shredded from 2cm down to 3mm.

11. RELEASE OF BLOWING AGENT FROM SHREDDED MATERIAL

The objective of the experiment was to quantify the amount of blowing agent released from shredded foam as a function of time during the six weeks following the shredding. The objective was met by performing flux chamber experiments using both real shredded foam from an industrial shredding installation and artificially shredded foam from the glove box experiment. The industrially shredded foam was collected at Aarhus Recycling Company. For information about Aarhus Recycling Company see Appendix 10. Two different size fractions of the collected shredded material were used in the flux chambers experiments while three different size fractions of artificially shredded material obtained from the glove box experiment were included. The experimental flux chamber set-up is described in section 8.1. Table 11.1 shows the conducted flux chamber experiments using shredded material. Table 11.1 also shows the total content of CFC-11 measured before shredding, see section 5.2 and 5.3 for foam sampling and analysis.

Table 11.1. The conducted flux chamber experiments using shredded material

Experiment	Size	mm	Total initial content of BA mg/cm^3	% w/w	Tool used for shredding
Shredded foam collected at Aarhus Recyling Company					
CFC-11	Large	8 - 16	3.49	10.1	Shredder
CFC-11	Medium	4 - 8	3.49	10.1	Shredder
Artificial shredded foam					
CFC-11	Large	8 - 16	3.43	13.3	Knife and hand
CFC-11	Medium	4 - 8	3.43	13.3	Grater
CFC-11	Small	2 - 4	3.43	13.3	Food blender

11.1 Release of BA from shredded foam collected at Aarhus Recyling Company

Figure 11.1 shows the "total loss" in percentage during six weeks from the shredded foam collected at Aarhus Recyling Company (not including instantaneous release during shredding). The total loss is calculated using the total initial amount of CFC-11 in the foam. This experiment shows the same trend as the previously mentioned experiment, i.e., that the largest share of the BA release happens within the first 200 hours, and that release decreases thereafter. The experiment shows roughly similar losses for both size fractions. The total loss is approx. 6.8% for the 4-8 mm foam particles, and a little higher 8.1% for the 6-16 mm foam particles.

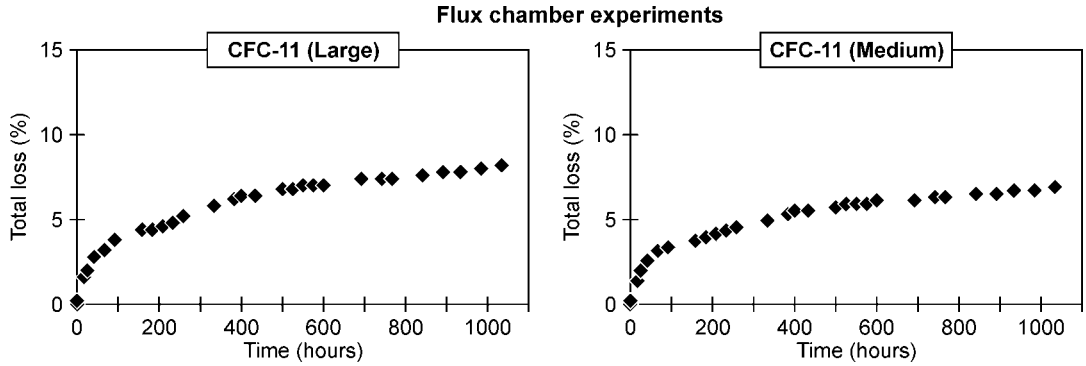


Figure 11.1. Total loss of CFC-11 in percentage of total BA content from shredded foam collected at Aarhus Recyling Company versus time. *This total loss does not include the instantaneous loss, which was lost during cutting previous to the start of the flux chamber experiment.*

11.2 Release of BA from artificially shredded foam

Figure 11.2 shows the total loss of CFC-11 in percentage from foam artificially shredded into three size fractions. The largest loss is experienced for the largest foam particles (12.5%). The smallest loss is observed for the mid-sized particles (8.5%), whereas the loss from the smallest particles is approx. 10.9%. The experiment does not show a general trend and the difference between the losses for the three size fractions is small. However, the experiment is coherent with the experiments carried out with foam shredded in real-life (industrial) conditions, especially when taken into account that: (a) the shredded particles are quite different in shape if not in size; and (b) the foam, which has been processed through the industrial shredding installation, has been crushed and compressed and may thereby have lost a larger part of the BA by the time it exits the shredding process.

The experiment does not show the expected and "conceptually right" results i.e., the smaller the foam particles the higher the loss. This might be because the loss is calculated using the total CFC-11 content in foam before shredding. The glove box experiment showed that a significant amount of BA is lost during shredding and the BA content in the shredded foam will therefore be lower than before shredding. The content in the smaller foam particles, when placed in the flux chambers, is expected to be lower than in the bigger foam pieces. Calculations of the total loss using the BA content after shredding would thus show a higher loss for the smaller foam particles due to a lower BA content, which would be more in line with the expected results. To do these calculations it would be necessary to analyse the content in the shredded foam.

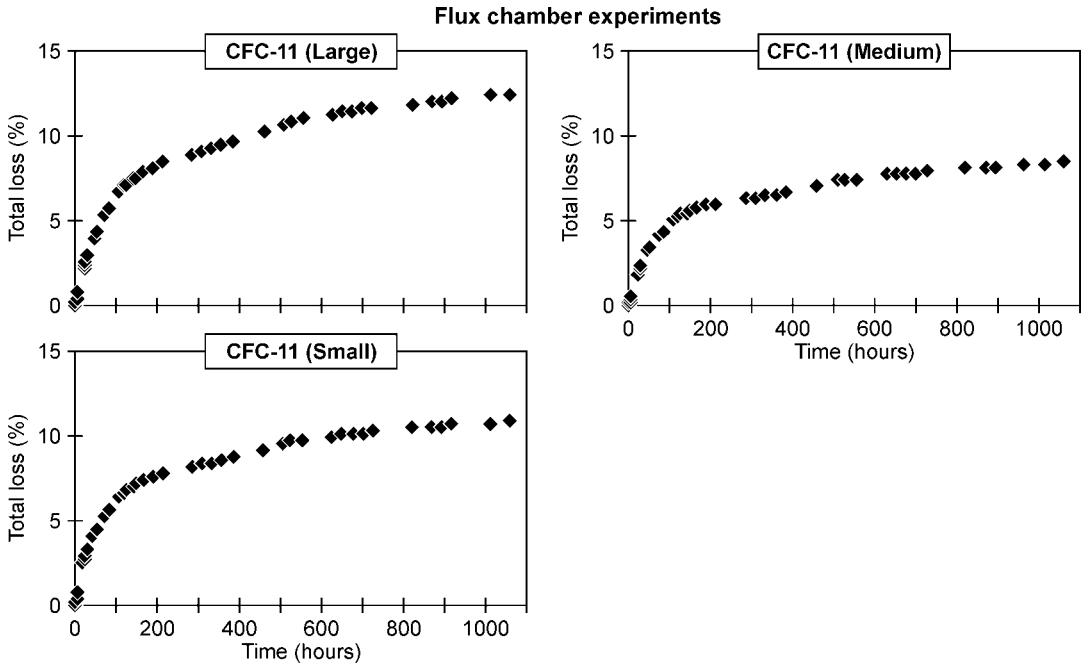


Figure 11.2. Total loss of CFC-11 in percentage from foam artificially shredded into three size fractions. The total loss does not include the instantaneous loss, which was lost during cutting previous to the start of the flux chamber experiment.

12. DISCUSSION

12.1 Comparison of methods for determining total content of blowing agent in foam

Two different methods have been used for determining total content of blowing agent in foam, a method based on heating and a method based on extraction with dimethyl formamide. Initial investigations of the two methods showed that only one step is needed to get almost all (approx. 99%) blowing agent out of the foam sample. The heating method gives slightly higher total contents for all four blowing agents, is relative easy to use, and does not imply the use of large volumes of a toxic chemical as the extraction method does. The heating method is therefore to be preferred.

Both methods as used in this project will probably underestimate the true total content of blowing agent in the foam panels. The glove box experiment (see section 10.2) clearly showed that there will be an instantaneous loss of blowing agent while cutting the foam specimen out of the panel. Based on the experiments investigating the dependency of the instantaneous loss to particle size, the loss for the specimen size used in the method used (cylinders of 1cm diameter and 1cm height) is estimated to approximately 15%. It should be emphasized that the original objective of this project was not to develop methods for determining total content of blowing agent. However if the true total content of the foam panels used is absolutely necessary, the panels must be analyzed with a technique including the instantaneous loss. This may be done by some commercially available laboratories, which may have developed such a method. It may alternatively be done using the described heating technique on a larger foam sample, which initially has been shredded in a glove box with simultaneous determination of the instantaneous release under the shredding process. By using a large foam sample (i.e. 10·10·5 cm) the BA loss due to cutting the sample would be insignificant compared to the total BA content of the sample.

12.2 Comparison of methods for measuring releases of blowing agent from shredded foam

Four different methods have been used for measuring the releases of blowing agent from shredded foam. The methods are:

- Infinite bath experiment using gravimetric method measuring weight loss over time
- Infinite bath experiment using extraction method measuring BA content in foam samples at different times
- Batch experiment measuring BA release from foam specimen to closed volume over time
- Flux chamber experiment measuring BA flux from a container with foam specimens through which a constant gas stream is maintained

Comparing the gravimetric method to the other methods it was clearly shown that there was a poor correlation of the weight loss to the loss of blowing agent. This is probably a result of uptake of other gases (oxygen, nitrogen and water vapor) and the release of carbon dioxide, which theoretically will be released with a higher rate than the BA. Thus, the gravimetric method cannot be recommended for measuring the BA loss from shredded foam.

The precision of the extraction methods relies on the possibility of producing a large number of foam specimens with exactly the same volume. Since the method is destructive, differences in specimen volume and initial BA content would scatter the results. By use of a cork bore to obtain precise specimens and triplicate extractions in combination with duplicate GC analysis, enough precision was obtained. The observed mass release/time curves were very similar to the results obtained from the flux chamber experiments. An alternative heating extraction method could have been applied to avoid the use of toxic chemicals in the laboratory.

The flux chamber experiment gave very good results. A control experiment showed that the fluxes from foam specimens contained in the flux chamber could be measured with high precision. The results even showed that closed cell diffusion coefficients could be determined within the six-week duration of the experiments. However, the experiment is time consuming and implies the use of special reduction valves and high precision pumps and gas flow meters.

As an alternative to the flux chambers simple batch experiments were used with a very high head-space to foam volume ratio to keep head-space concentration so low that the diffusion gradients theoretically should be close to unaffected by the accumulating BA concentration in the closed container. However, the release rates in the batch experiment were generally lower than the release rates obtained from the flux chamber experiments for all types of BAs. The reason for this has not been found, but may be due to the different concentration ranges in the two experiments.

Overall, the flux chamber method seems to provide the most reliable results, but is quite laborious. The batch method is simpler and provides a fair evaluation of the BA mass released after shredding. However, this method seems to slightly underestimate the release. The reason for this has not been found.

12.3 Evaluation of release phases

The performed BA release experiments clearly showed that releases followed three phases after shredding/cutting: an instantaneous release phase, an short-term release phase, and a long-term release phase. A conceptual model may be setup explaining this general observation: By cutting the foam, a proportion of the cells is either split or damaged to a degree allowing for a sudden release of the contained atmosphere in the cell (*the instantaneous release*). Cells adjacent to the cut surface may be only slightly damaged by tiny cracks or holes allowing a relative slow release of BA to the surroundings (*the short-term release*). A significant portion of the cells in the foam particle will be unaffected and only allow release governed by slow diffusion through the PUR cell wall (*the long-term release*). The simulations by the double compartment model on the performed experiments showed that the short-term release has a typical duration of up to 400 hours for the particle sizes used in the experiments.

13. PERSPECTIVES

13.1 Estimating of the instantaneous loss during shredding

The amount of blowing agent released during shredding can be estimated using the results obtained in the glove box experiment, the information on size fractions of the shredded foam, and the total initial content of BA in foam. Table 13.1 shows the parameters used for the estimation. Assuming that a foam sample of 1000 g with a total BA content of 10%w/w is shredded in a shredder similar to the shredder at Aarhus Recycling Company a total loss of 18 to 24% is expected. Table 13.1 also shows the mass loss of BA from the different size fractions. Even though only a small part (< 4%) of the foam particles are smaller than 0.5 mm, this fraction might contribute significantly to the instantaneous release during shredding. Since the smallest particle size obtained in the glove box experiment was 2-4 mm a conservative loss of 38.7% is assumed in the calculations for particles smaller than 2 mm. However the loss from particles smaller than 2mm is expected to be significantly higher, meaning the calculated total loss is underestimated.

Table 13.1. Total instantaneous loss of BA from a foam sample of 1000 g from with a total content of 10%w/w.

		Sample A			**Sample B**		
Size	**Loss (a)**	**Fraction (b)**	**Total mass of foam**	**Instant. loss of BA**	**Fraction (b)**	**Total mass of foam**	**Instant loss of BA**
mm	%	%	g	g	%	g	% w/w
< 1	38.7	9.7	97	3.8	3.5	35	1.3
1 to 2	38.7	3.9	39	1.5	0.3	3	0.1
2 to 4	38.7	7.8	78	3.0	1.3	13	0.5
4 to 8	33.8	19.7	197	6.7	10.0	10	3.4
8 to 16	17.6	42.9	429	7.6	54.5	545	9.6
16 to 32	9.4	15.9	159	1.5	30.4	304	2.9
Total		100	1000	24.0	100	1000	17.8

(a): Total loss from foam according to sizes - results obtained from the glove box experiment
(b): Share of particles of a specific size (by weight) in the sample - based on size analysis of shredded foam collected at Aarhus Recycling Company (see section 5.5).

13.2 Estimating the future releases of halocarbons from decommissioning used refrigerator/freezers in the United States

Based on the laboratory experiments presented in the previous chapters the future releases of halocarbons from decommissioning used refrigerator/freezers (R/Fs) in the United States will be estimated. The evaluation will be carried for R/Fs produced in the period 1985-2010. The following input data is needed to perform the estimation:

1. Numbers of R/Fs produced in the USA from 1985 until now.
2. An estimation of the expected US production of R/Fs until 2010
3. An estimate of the types of BA used as a function of year

4. Typical lifetime of a unit
5. Typical foam volume per unit and BA weight fraction in foam
6. Release patterns (instantaneous, short and long term releases) from foam after decommissioning, i.e. the fraction of BA for one unit released for each year following the decommissioning

***Re 1 and 2*:** Figure 13.1 shows the numbers of R/Fs produced for each year in the period 1985-2010[22]. The values from 2003 and on are based on a 3% growth in production each year. Any import or export of unit to and from the United States is neglected. The numbers are given in Appendix 12.

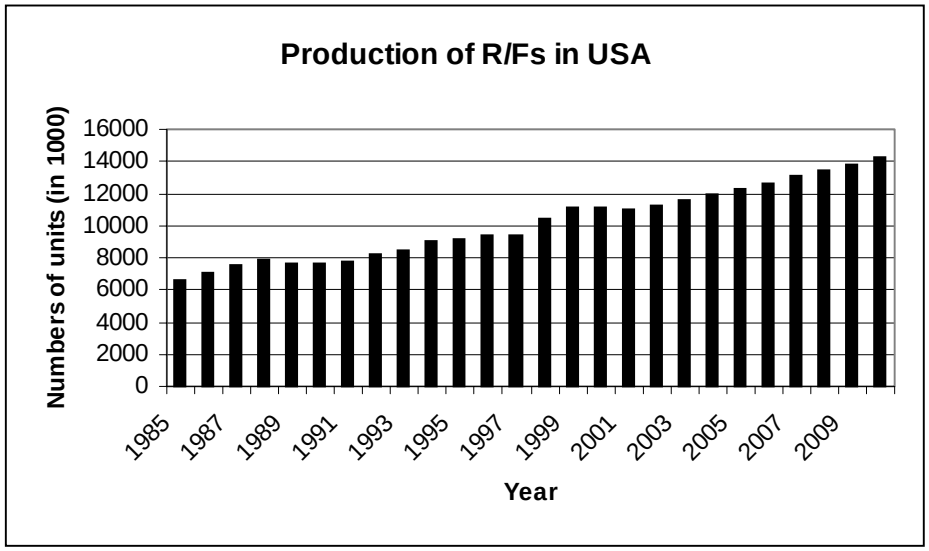


Figure 13.1 Production of refrigerators and freezers in United States for each year in the period 1985-2010.

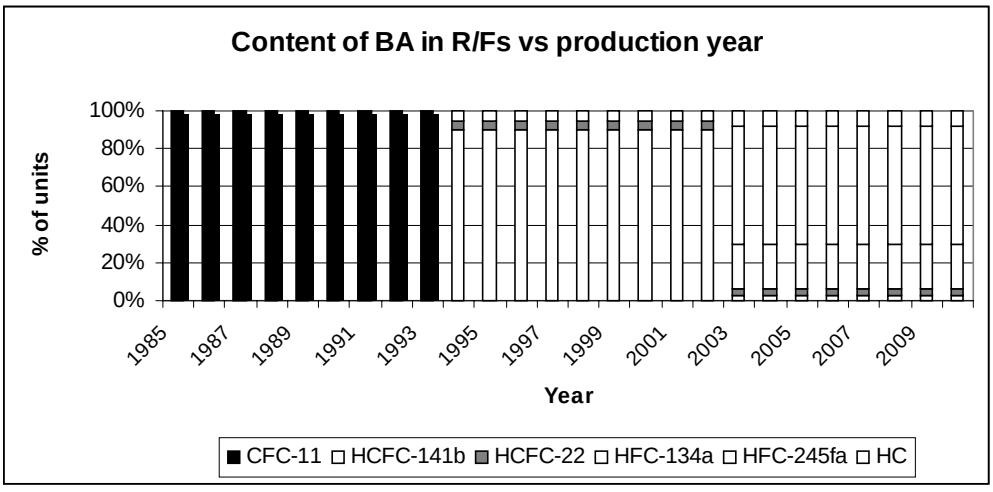


Figure 13.2 Blowing agents used in US R/Fs in the period 1985-2010. HC=hydrocarbon.

***Re 3*:** Figure 13.2 gives an estimated on the type of blowing agent which was/will be used in R/Fs in the USA[22] in the period 1985-2010. Numbers are given in Appendix 11.

***Re 4*:** A fixed lifetime of 15 years is assumed. In a second version of the models it could be interesting to incorporate a lifetime distribution instead. However, at the moment such data is not available[22].

***Re 5*:** The foam volume per unit was set to 10 ft^3/unit[22] equal to 283 L/unit. The BA foam weight fractions and foam densities are given in Table 13.2. These numbers are typical numbers valid for the foam panels used in the experiments performed in this project (confer chapter 6).

Table 13.2 Foam density and BA content used in the model. The values are based on the determined values.

	CFC-11	HCFC-141b	HFC-134a	HCFC-22	HFC-245fa
Foam density (g/L)	25	32	39	25	31
BA content (%w/w)[1]	15.3	13.3	8.1	15.0	13.3
BA content (g/unit)[2]	1083	1209	889	1062	1171

1: 15% added to measured total content to account for instantaneous loss, which is not accounted for with the used method.

2: using the foam content of 283 L/unit and the determined foam densities.

***Re 6*:** This project has shown that the release patterns of blowing agent from the foam to a high degree depend on how the home appliances are being decommissioned. If the foam is shredded into very fine particles the release is fast and nearly all blowing agent is released within a short period. On the other hand the release may be slow if the foam is cut into larger pieces. To evaluate the significance on the shredding process, three scenarios are selected:

1. Shredding Scenario A: Foam is shredded as in the Danish recycling facility (Danish Recycling Center)
2. Shredding Scenario B: Foam is shredded to a more coarse particle distribution
3. Shredding Scenario C: Foam is cut into larger pieces with dimensions close to typical foam thicknesses in R/F units

Based on the results from the experiments the BA fractions, which will be released instantaneously, over short term and over long term, respectively, are estimated for each of the foam particle size categories used in the size distribution. The particle size distribution of the three different shredding scenarios are given in Table 13.3 while the estimated release category fractions are given in Table 13.4.

Table 13.3 Particle size distribution in the three Shredding Scenarios.

	Particle size category				
	<4mm	4-8mm	8-16mm	16-32mm	>32mm
Shredding scenario A					
Percentage of foam (%w/w)	14.5	15	48.1	22.4	0
Shredding scenario B					
Percentage of foam (%w/w)	5	15	15	45	20
Shredding scenario C					
Percentage of foam (%w/w)	2	3	5	15	75

Table 13.4 The fractional distribution of the instantaneous, short-term and long-term releases as a function of foam particle size.

	Particle size category				
	<4mm	4-8mm	8-16mm	16-32mm	>32mm
Instantaneous release (%w/w)	40	34	18	10	5
Short-term release (%w/w)	60	40	10	4	2
Long-term release (%w/w)	0	26	72	86	93

The instantaneous and short-term releases are allocated to the year where the unit is decommissioned. For the long-term release the particles are assumed cylindrical. For instance for particles in the 8-16 mm range, the particles are assumed cylindrical with a radius of 12 mm and a height of 12 mm. For the largest fraction a diameter/height of 40 mm is assumed, since most foam particles originating from a R/F will have a maximal dimension of approx. 48 mm. For the smallest fraction it is assumed that the long-term release is insignificant.

The release-time dependency (grams BA released per year per unit) is calculated by equations 3 and 5 in chapter 3. After calculating the fraction of the initial mass released (M_t/M_0) for each year, the release for one single year is calculated by subtracting M_t/M_0 calculated for two succeeding years, and multiplying by the mass of blowing agent in the particle range category in question, and finally summing up all five particle size categories. For simplification the long-term diffusion coefficient is set to $2.0 \cdot 10^{-14}$ m^2/s for all five BAs, since the flux chamber experiments only find minor differences in diffusion coefficient among BAs. The dependency is calculated for a 50 year time period after decommissioning. Figure 13.3 is an example of the calculated release-time dependency for a unit blown with CFC-11. Due to the rather extensive calculations the releases are interpolated after the first 15 years for periods of 10 years. This simplification has no significant effect on the final calculated releases. For scenario A almost all of the BA is released over the 50 year period (i.e., 97.7%). However, for the scenario B and C, the release over the 50 year period is 88.8% and 73.8%, respectively.

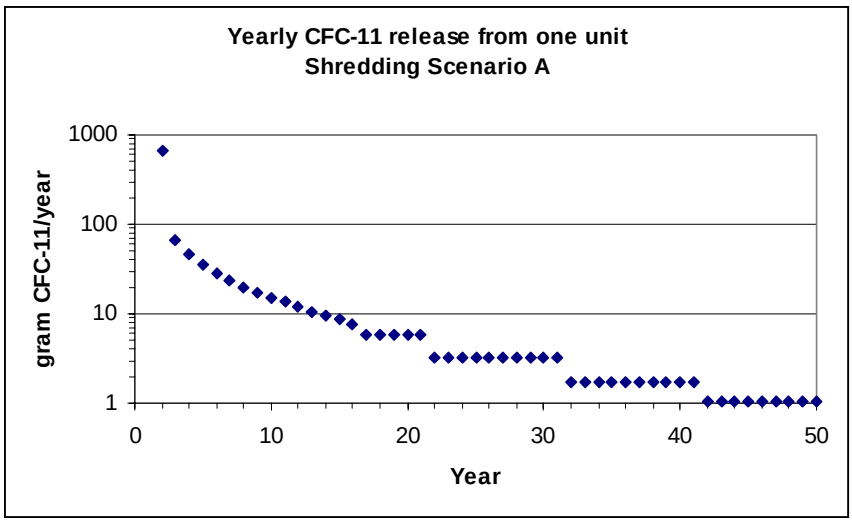
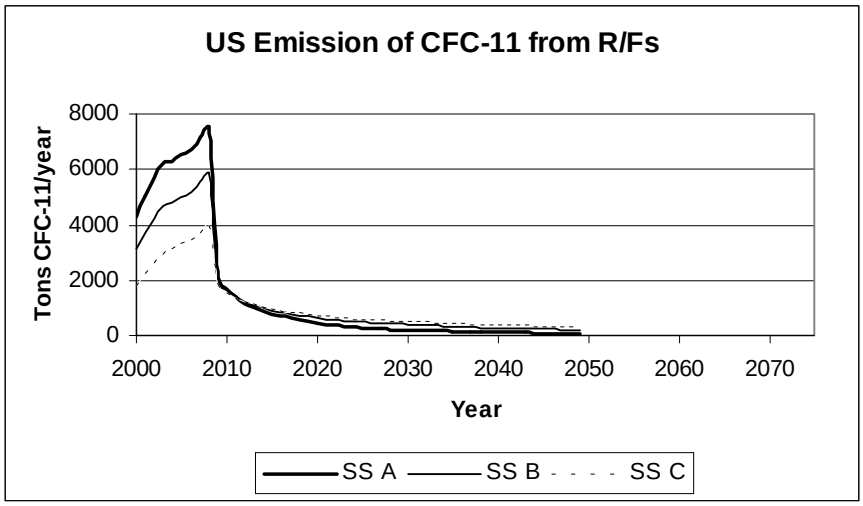


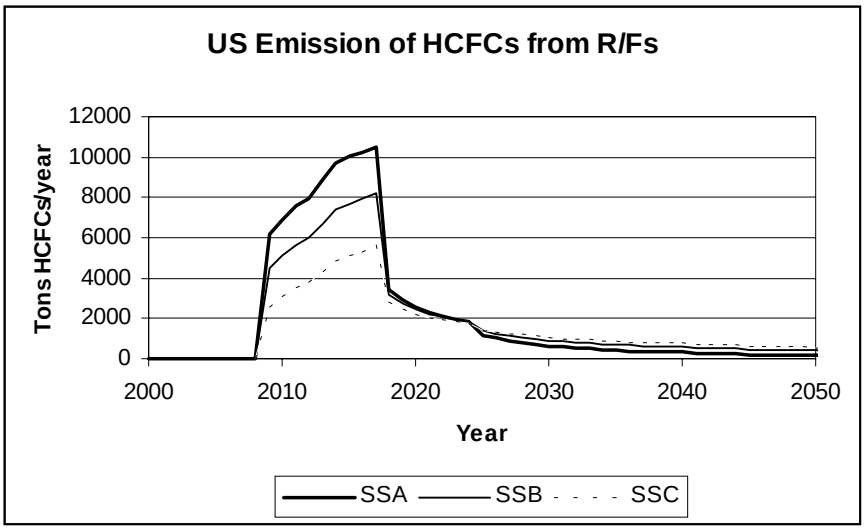
Figure 13.3 The yearly release of CFC-11 from one unit as a function of year after decommissioning assuming that the unit is shredded according to Shredding Scenario A (confer Table 13.3)

From data as presented in Figure 13.3 the total yearly release for a specific BA is calculated by adding up contributions from units decommissioned the specific year and from the previous years´ decommissioned units.

The result of the modeling is presented in Figures 13.4a-e for the five blowing agents. The BA emissions are given in tons BA/year. *It should be emphasized that the emissions are only related to decommissioning of the R/Fs produced in the period 1985-2010*. The figures show that the magnitude of the peak emissions are very much dependant on how the shredding is carried out. For scenario B and C a small but significant fraction of the release will take place after the 50 year period.

The model assumes that the long-term releases from the foam waste after disposal at landfills are still governed by closed cell diffusion behavior. Due to mechanical forces within the landfilled waste, the foam structure may be further damaged leading to faster releases. The model also assumes that all BA released from the foam particles is readily emitted, and do not take into account any attenuation of BA in the landfill or the soil covers surrounding the landfill, which may lead to reduced emissions.





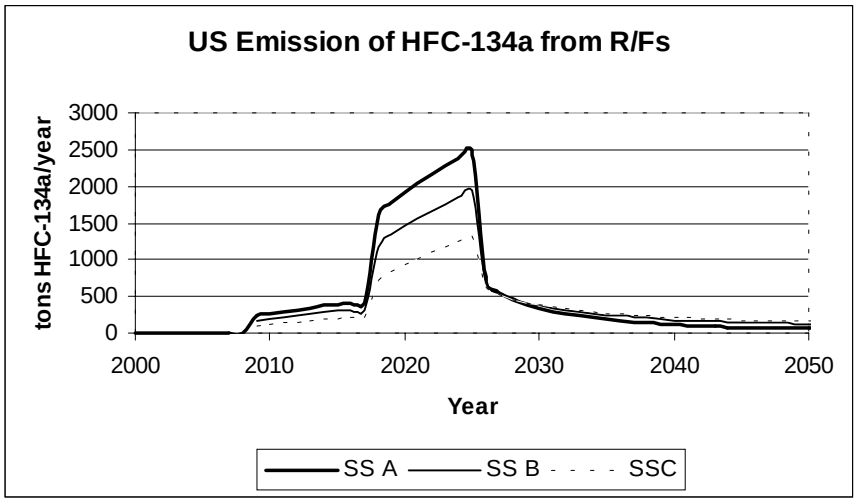


Figure 13.4 a-c. Results of the emission model for the three different shredding scenarios for the blowing agents, CFC-11, HCFC-141b, and HCFC-22 (pooled in figure 13.4b as HCFCs), and HFC-134a.

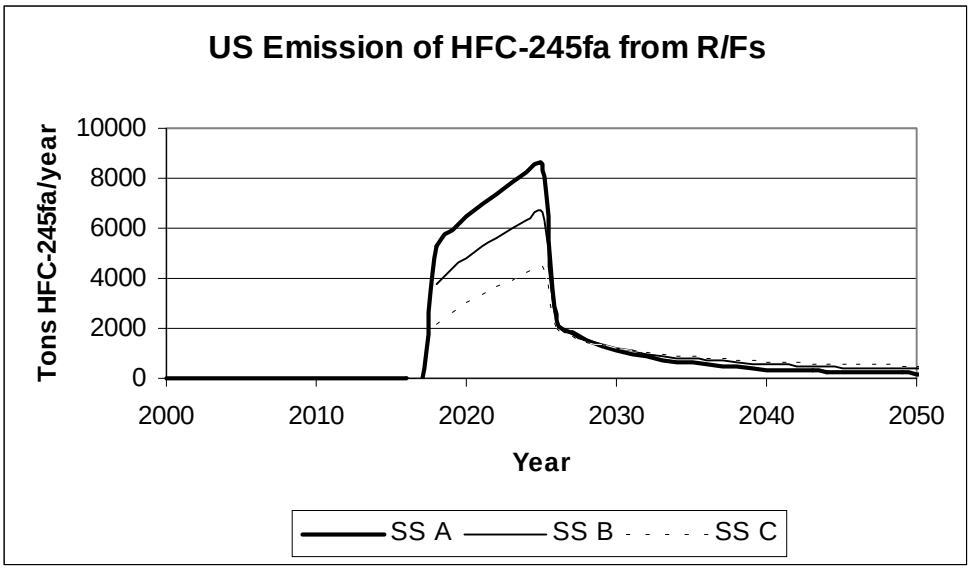


Figure 13.4d Results of the emission model for the three different shredding scenarios for the blowing agent HFC-245fa.

14. IDEAS FOR FURTHER/RELATED RESEARCH

This project indicated a significant difference in BA releases among producers. However, the results could not give a final answer to how important this is. Only further release studies using more foam panels from different producers can elucidate this.

If no recycling facilities will be used in the future to reduce the foam related halocarbon emissions during shredding, the instantaneous and the short-term releases must be assumed to be emitted directly to the atmosphere. The residual content will end up in landfills. The fate of different halocarbons in the landfill after disposal is not known in much detail. The following questions could be raised:

- Would the long-term release from the foam waste still be controlled by closed cell diffusion behavior, or would the foam be further mechanical affected (leading to enhanced releases)?
- What are typical degradation rates of the halocarbons within the landfill?
- Would there be formed toxic degradation products in the landfill?
- How significant would the soil attenuation in soil covers be to halocarbons emitted from the waste body?

15. REFERENCES

1 U.S. Environmental Protection Agency. Protecting the Ozone Layer: Safe Disposal of Home Appliances Containing Ozone-Depleting Substances. Air and Radiation, Report EPA 430-K-93-001. **1993**.

2 Brandreth, D.A.; Ingersoll, H.G. *Journal of Cellular Plastics*. **1980**. July/Aug., 235-238.

3 Norton, F.J. *Journal of Cellular Plastics*. **1982**, Sept./Oct., 300-318.

4 Ostrogorsky, A.G.; Glicksman, L.R. *Journal of Heat Transfer – Transactions of the ASME.* **1988**, 110, 500-506.

5 Bart, G.C.J.; Du Cauzé de Nazelle, G.M.R. *Journal of Cellular Plastics.* **1993**, 29, 29-42.

6 Hong, S.; Duda, J.L. *Journal of Applied Polymer Science.* **1998**. 70, 2069-2073.

7 Alsoy, S. *Journal of Cellular Plastics.* **1999**, 35, 247-271.

8 Kjeldsen, P.; Jensen, M.H., Release of CFC-11 from disposal of polyurethane from waste. *Environmental Science and Technology* **2000, 35, 3055-3063**.

9 Crank, J. *The Mathematics of Diffusion,* Clarendon Press, Oxford, UK, 1975, 414pp.

10 Grathwohl, P. *Diffusion in Natural Porous Media: Contaminant Transport, Sorption/Desorption and Dissolution Kinetics,* Kluwer Academic Publishers, Boston, 1998, 207pp.

11 Hong, S.U.; Albouy, A.; Duda, J.L. *Journal of Applied Polymer Science*, **2001**, 79, 696-702.

12 Dement'ev, A.G.; Khlystalova, T.K.; Zinger, P.A. Diffusion of foaming agents and prediction of the characteristics of polyurethane foams during aging. ??

13 Fan, Y; Kokko, E. *Journal of Cellular Plastics*, **1995**, 31, 532-547.

14 Wu, J.; Albouy, A.; Mouton D. *Journal of Cellular Plastics*, **1999**, 35, 421-437.

15 Bhattacharjee, D.; Booth, J.R. *Journal of Cellular Plastics*, **1995**, 31, 244-259.

16 U.S. Environmental Protection Agency Homepage, http://www.epa.gov/region04/air/cfc/applianc.htm

17 Gamlen, P.H.; Lane, B.C.; Midgley, P.M. *Atmospheric Environment*, **1986**, 20(6), 1077-1085.

18 Khalil, M.A.K.; Rasmussen, R.A. *JAPCA.* **1986**, 36, 159-163.

19 Bomberg, M.T.; Lstiburek, J.W. Spray Polyurethane Foam in External Envelopes of Buildings. Technomic **1998** (ISBN: 1-56676-707-5)

20 Svanström, M.; Ramnäs, O. *Journal of Cellular Plastics.* **1993**, 32, 159-171.

21 Bartlett, P.L.; Creazzo, J.A.; Hammel, H.S. *Journal of Cellular Plastics.* **1994**, 30, 126-142.

22 Larry Weitje, Personal communication, AHAM.

23 Bomberg & Kumaran (**1989**) in Bomberg, M.T. & Lstiburek, J.W. Spray Polyurethane Foam in External Envelopes of Buildings. 1998 Technomic (ISBN: 1-56676-707-5)

24 Bomberg & Brandreth (**1990**) in Bomberg, M.T. & Lstiburek, J.W. Spray Polyurethane Foam in External Envelopes of Buildings. 1998 Technomic (ISBN: 1-56676-707-5)

DETERMINATION OF THE FRACTION OF BLOWING AGENT RELEASED FROM REFRIGERATOR/FREEZER FOAM AFTER DECOMMISSIONING THE PRODUCT

APPENDICES

Appendix 1

Measurements of the total content of blowing agent and carbon dioxide in the four different foam panels based on the heating method.

Foam	Blowing agent		Carbon dioxide		Total	
	mg/cm^3	% w/w	mg/cm^3	% w/w	mg/cm^3	% w/w
CFC-11	3.58	14.53	0.17	0.71	3.75	15.24
	3.66	14.87	0.15	0.74	3.81	15.61
	3.50	14.22	0.13	0.68	3.63	14,90
	3.35	13.61	0.13	0.69	3.48	14.30
HFC-134a	2.97	7.62	1.71	4.56	4.68	12.18
	2.91	7.46	1.87	4.96	4.78	12.42
	2.85	7.30	1.87	5.05	4.72	12.35
	2.81	7.21	1.81	4.86	4.62	12.06
HCFC-141b	4.93	15.29	0.90	2.97	5.83	18.26
	4.24	13.17	0.94	3.05	5.18	16.22
	4.47	13.87	0.86	2.83	5.33	16.70
	4.73	14.67	0.86	2.85	5.59	17.52
HFC-245fa	3.57	11.63	0.51	1.96	4.08	13.58
	3.39	11.04	0.58	2.19	3.98	13.23
	3.10	10.07	0.46	1.78	3.55	11.85
	3.32	10.78	0.53	2.04	3.84	12.82

Foam	Blowing agent		Carbon dioxide		Total	
	mg/cm^3	% w/w	mg/cm^3	% w/w	mg/cm^3	% w/w
CFC-11	2.93	11.90	0.14	0.57	3.08	12.48
	3.17	12.88	0.12	0.48	3.29	13.36
	2.87	11.63	0.13	0.54	3.00	12.17
	3.43	13.92	0.12	0.50	3.55	14.43
HFC-134a	2.55	6.54	1.63	4.19	4.18	10.72
	2.73	7.01	1.65	4.23	4.38	11.25
	2.49	6.38	1.87	4.79	4.35	11.17
	2.83	7.27	1.74	4.46	4.57	11.73
HCFC-141b	4.22	13.09	0.84	2.61	5.06	15.71
	3.43	10.65	0.87	2.71	4.30	13.36
	3.28	10.17	0.88	2.72	4.15	12.89
	2.12	6.58	0.79	2.45	2.91	9.03
HFC-245fa	3.51	11.42	0.59	1.92	4.10	13.34
	3.18	10.33	0.56	1.82	3.73	12.15
	3.37	10.95	0.55	1.79	3.91	12.73
	3.62	11.77	0.51	1.67	4.13	13.44

Foam	Blowing agent		Carbon dioxide		Total	
	mg/cm^3	% w/w	mg/cm^3	% w/w	mg/cm^3	% w/w
CFC-11	3.15	12.78	0.11	0.44	3.26	13.22
	3.43	13.90	0.09	0.37	3.52	14.27
	3.06	12.43	0.13	0.54	3.20	12.97
	3.29	13.33	0.22	0.89	3.50	14.22
HFC-134a	2.48	6.36	1.63	4.18	4.11	10.54
	2.66	6.83	1.65	4.22	4.31	11.05
	2.42	6.21	1.86	4.78	4.28	10.99
	2.76	7.08	1.73	4.45	4.49	11.52
HCFC-141b	3.55	11.00	0.67	2.07	4.21	13.07
	3.73	11.57	0.69	2.15	4.42	13.71
	3.58	11,12	0.69	2.15	4.28	13.27
	3.21	9.95	0.98	3.05	4.19	13.00
HFC-245fa	3.62	11.79	0.59	1.91	4,21	13.70
	3.44	11.19	0.55	1.80	3,99	12.99
	3.53	11.50	0.54	1.77	4,08	13.27
	3.96	12.88	0.51	1.65	4,47	14.54

Foam	Blowing agent		Carbon dioxide		Total	
	mg/cm^3	% w/w	mg/cm^3	% w/w	mg/cm^3	% w/w
CFC-11	3.68	13.02	0.16	0.55	3.83	13.58
	3.61	13.00	0.16	0.58	3.77	13.58
	4.00	13.24	0.15	0.51	4.15	13.75
	4.08	13.92	0.14	0.49	4.22	14.42
	3.59	12.99	0.16	0.57	3.75	13.56
HFC-134a	3.15	6.77	0.76	1.63	3.91	8.40
	2.81	7.09	0.86	2.16	3.67	9.24
	2.96	6.96	0.92	2.16	3.88	9.12
	2.82	7.59	0.94	2.53	3.76	10,12
	3.06	7.84	0,95	2.43	4.01	10.26
HCFC-141b	4.11	12.48	0.55	1.68	4.66	14.16
	3.33	10.20	0.53	1.62	3.86	11,82
	4.12	11.64	0.62	1.75	4.74	13.39
	3.96	12.29	0.50	1.56	4.46	13.85
	3.14	9.77	0.50	1.56	3.64	11.34
HFC-245fa	4.42	13.45	0.33	0.99	4.75	14.44
	3.96	11.97	0.35	1.06	4.31	13.03
	4.37	12.63	0.35	1.00	4.72	13.63
	4.28	12.65	0,34	1.00	4.62	13,65
	3.64	11.42	0.34	1.06	3.97	12.49

Average and standard deviation

Foam	Blowing agent		Carbon dioxide		Total	
	mg/cm^3	% w/w	mg/cm^3	% w/w	mg/cm^3	% w/w
CFC-11	3.43 (0.34)	13.30 (0.88)	0.14 (0.03)	0.58 (0.13)	3.58 (0.35)	13.98 (0.92)
HFC-134a	2.78 (0.21)	7.03 (0.47)	1.50 (0.42)	3.86 (1.16)	4.28 (0.35)	10.89 (1.17)
HCFC-141b	3.77 (0.69)	11.62 (2.11)	0.75 (0.16)	2.34 (0.56)	4.52 (0.73)	13.96 (2.33)
HFC-245fa	3.66 (0.40)	11.62 (0.90)	0.48 (0.10)	1.61 (0.41)	4.14 (0.34)	13.23 (0.71)

Appendix 2

Measurements of the total content of blowing agent and carbon dioxide in the four different foam panels based on the solvent extraction method.

Foam	Blowing agent	
	mg/cm^3	% w/w
CFC-11	3.99	13.63
	4.01	13.73
	4.17	14.27
	3.97	13.60
	4.07	14.39
	3.77	13.35
HFC-134a	2.15	5.36
	2.19	5.44
	1.89	4.54
	1.87	4.48
	2.14	4.27
	1.98	3.96
HCFC-141b	4.10	11.94
	3.77	10.98
	4,04	12.50
	4.29	13.27
	3.38	10.36
	3.82	11.71
HFC-245fa	4.08	11.95
	4.18	12.24
	4.32	13.71
	3.27	10.37
	3.63	11.11
	3.55	10.88

Blowing agent	
mg/cm^3	% w/w
3.91	13.17
4.91	16.56
3.42	11.66
3.06	10.45
4.33	15.43
3.67	13.05
2.10	5.31
2.14	5.41
2.45	5.52
2.39	5.37
2.36	5.52
2.24	5.23
3.07	8.73
2.81	7.99
3.83	11.77
4.22	12.96
4.22	12.53
4.31	12.79
3.95	12.04
3.87	11.79
4.04	12.24
4.01	12.15
3.47	10.62
3.57	10.92

Foam	Blowing agent	
	mg/cm^3	% w/w
CFC-11	2.91	11.80
	2.54	10.33
	2.98	12.10
	3.18	12.91
HFC-134a	2.50	6.42
	2.82	7.24
	2.61	6.70
	2.87	7.38
HCFC-141b	3.77	11.70
	3.90	12.11
	3.71	11.50
	3.41	10.57
HFC-245fa	4.30	14.00
	4.14	13.46
	3.85	12.51
	4.01	13.03

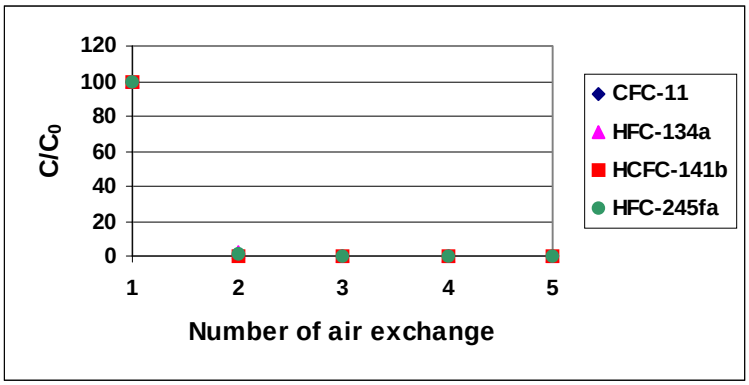
Foam	Blowing agent	
	mg/cm^3	% w/w
CFC-11	2.85	9.64
	2.70	9.13
	3.07	10.41
	3.12	10.57
	3.43	12.28
	3.00	10.74
	2.89	10.35
	2.89	10.33
	4.29	15.94
	4.41	16.37
	3.16	11.74
	3.08	11.45
HFC-134a	2.28	5.24
	2.28	5.24
	2.34	5.49
	2.37	5.57
	2.49	5.88
	2.59	6.10
HCFC-141b	3.41	10.29
	3.17	9.57
	2.78	8.39
	3.03	9.15
	3.11	9.32
	3.25	9.73
	3.61	10.81
	3.30	9.87
	3.12	9.12
	3.66	10.71
	3.40	9.93
	3.30	9.65
HFC-245fa	3.37	10.57
	3.35	10.53
	3.28	10.30
	3.35	10.53
	3.21	10.10
	3.20	10.06
	3.15	9.88
	3.09	9.72
	3.84	11.91
	3.58	11.12
	3.81	11.83
	3.50	10.85

Average and standard deviation

Foam	Blowing agent	
	mg/cm^3	% w/w
CFC-11	3.49 (0.62)	12.48 (2.08)
HFC-134a	2.32 (0.26)	5.53 (0.86)
HCFC-141b	3.56 (0.45)	10.71 (1.47)
HFC-245fa	3.68 (0.37)	11.44 (1.19)

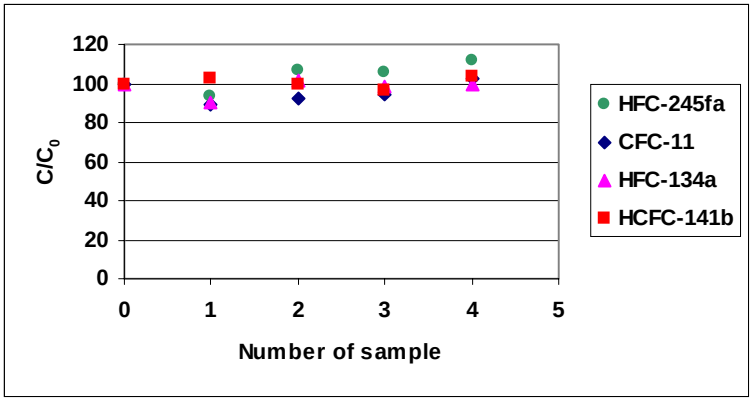
Appendix 3

Examination of the effectiveness of the heating procedure to drive out halocarbons from PUR.

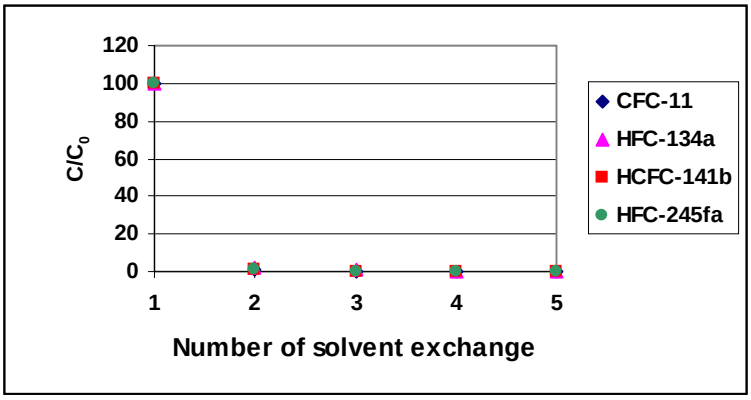


Appendix 4

A: Examination of sufficient extraction time.



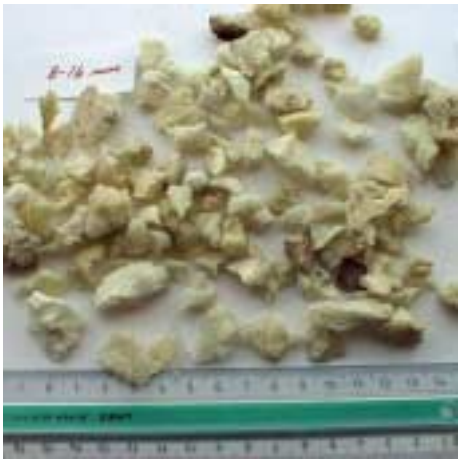
B: Examination of the effectiveness of the solvent to extract halocarbons contained in PUR.



Appendix 5

Shredded foam collected at Aarhus Recycling Company separated into six particle size fractions

Size 16 - 32 mm



Size 8 - 16 mm

Size 4 - 8 mm

Size 2 - 4 mm

Size 1 - 2 mm

Size < 1 mm

Appendix 6

Results from batch release experiments second round.

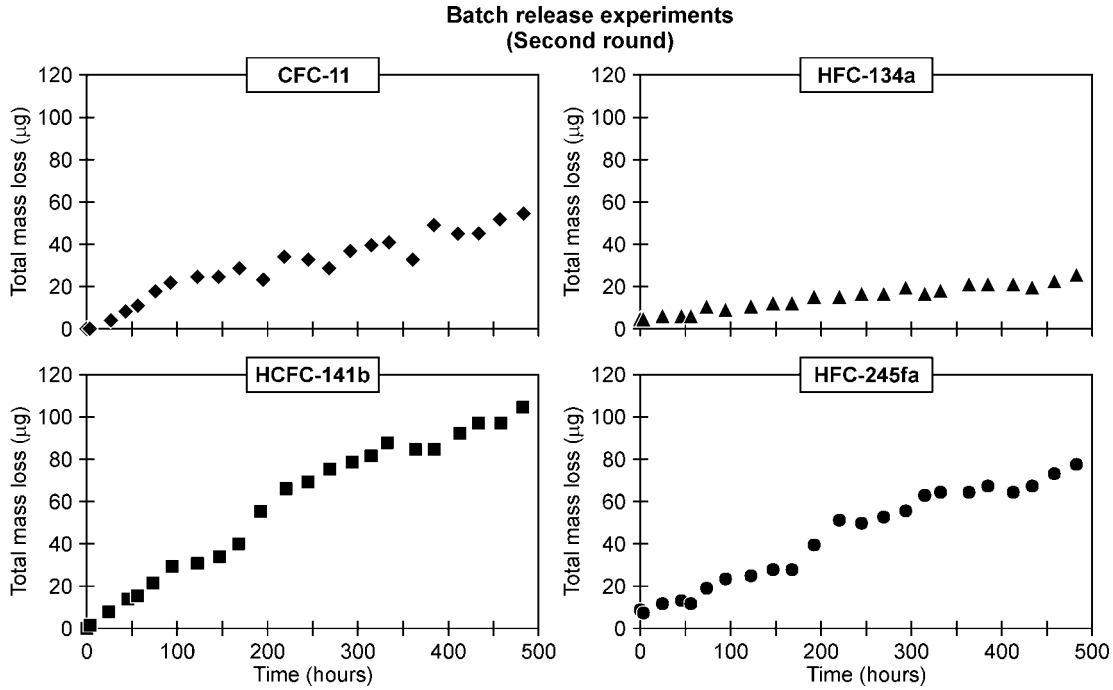


Figure. Results from batch release experiments second round where glass containers had been opened, emptied of gas and closed again. The release of blowing agent from foam blown with four different blowing agents.

Table. Comparison of release rates between batch experiments from first and second round. The obtained rates from the batch experiments carried out in the first round are calculated using the data from 450 to 1100 hours.

Batch release experiment - first round		**Batch release experiment - second round**	
Max. mass loss	**Rate**	**Max. mass loss**	**Rate**
µg	**µg/hour**	**µg**	**µg/hour**
450	0.10	58	0.11
250	0.10	28	0.04
660	0.17	114	0.22
650	0.16	85	0.15

Appendix 7

Experimental set-up of flux chambers

Appendix 8

Glove box used in the instantaneous release experiment

Glove box

Artificially shredded foam (Size fraction: 8-16mm)

Grater used for foam shredding (Size fraction: 4-8 mm)

Appendix 9

Artificially shredded foam

Artificially shredded foam using a knife and hand breaking (size fraction: 16-32 mm)

Artificially shredded foam using a grater (Size fraction: 4 - 8 mm)

Appendix 10

Århus Genbrugsselskab A/S

The investigation was carried out in collaboration with Århus Genbrugsselskab A/S (Aarhus Recycling Company), which has an encapsulated installation especially designed for the shredding of refrigerators and freezers.

Århus Genbrugsselskab A/S is a Danish company dealing with recuperation and recycling of raw materials from various waste categories. The company has its operations in Trige, just north of Århus in Denmark, where they have installations handling waste such as electronics, glass, plastics, paper and refrigerators/freezers.

Handling of the refrigerators and freezers

From the county recycling stations and from industry, Århus Genbrugsselskab receives refrigerators and freezers that have been discarded and that need to be disposed of in an environment-friendly way. The company is authorized to handle CFC gasses.

Århus Genbrugsselskab has more than 10 years experience with collection and environment-friendly disposal of refrigerators and freezers. On February 1, 2001, the CFC department inaugurated a new air treatment installation for the collection and handling of CFC gasses from the insulating foam in refrigerators and freezers. The installation is the first of its kind in the world, and uses catalytic air treatment to collect and destroy CFC gasses.

The process is based on very large quantities of gas-containing air being extracted directly from the shredding installations where the CFC gasses are released from the foam. The gas-containing air is then transported in a closed pipe system to a Catalytic Abator installation, where the CFC gasses are transformed into 12% salt water.

Every year between 200,000 and 300,000 refrigerators and freezers are discarded in Denmark, and Århus Genbrugsselskab A/S handles about 70,000 of them. In a couple of years the company projects to handle up to 100,000 units a year, which is the installation's capacity. The company has an agreement with Bresch Entsorgung GmbH from Neumünster (Germany), which handles additional 69,000 Danish units. Various waste companies throughout Denmark are handling the rest of the discarded refrigerators and freezers.

Sorting and breaking up of the refrigerators and freezers

When the units are received at Århus Genbrugsselskab A/S they are registered and sorted, after which the CFC-containing oil from the refrigeration circuit is recuperated and stocked. After that plastic, metal and glass parts are separated for subsequent recycling. The rest of the unit is then shredded and separated into recyclable fractions iron, cupper/aluminium and a combustible fraction (foam). The CFC released during the shredding process is recuperated and destroyed by the Catalytic Abator installation. The whole process is conducted according to the norms set by the Danish Environment Agency, i.e., at least 80% of all CFC in the refrigerator or freezer unit has to be recuperated and destroyed.

Appendix 11

Date:_____

Questionnaire for information on handling of used freezers/refrigerators

Name and location of region covered by this questionnaire:

Name and affiliation of person filling out this questionnaire:

Do laws/regulations exist in the region for the disposal, reuse or recycling of used freezers/refrigerators (F/R)?

If yes, does the laws/regulations cover the handling of insulation foam blown with fluorocarbons contained in the used F/Rs ?

Please give a short description of the laws/regulations:

How many used freezers/refrigerators are disposed of or recycled at the end of useful life in the region on a yearly basis?

How are used freezers/refrigerators handled in the region:

☐ Together with other bulky waste (%)

☐ Together with other secondary materials/obsolete consumer products containing metal in scrap recycling yards for metal recycling (%)

☐ In special facilities for used freezer/refrigerators (%) (if marked, how many facilities in the region?: _____)

☐ At a landfill where CFCs are recovered and capacitors are removed (%)

☐ Other (please specify:

_____

_____

_____

_____)

☐ Unknown

How is the foam insulation handled? (if more options are used in the region, please specify percentages):

☐ Direct landfilling (landfilling of whole freezers/refrigerator units (%)
☐ Foam is shredded, then landfilled (%)
☐ Foam is shredded, then incinerated (%)
☐ Units are broken down in larger pieces, then incinerated (%)
☐ Units are broken down in larger pieces, then landfilled (%)
☐ Shipped with whole freezer/refrigerator to scrap recycling facility (%)
☐ Foam insulation is reused (%) (if marked, please specify how):

_____
_____
_____
_____
_____

☐ Other (if marked, please specify):

_____
_____
_____
_____
_____

☐ Unknown

If the region has special facilities for handling used freezers/refrigerators:

Please specify what is done for minimizing emissions of fluorocarbons from insulation foam:

_____
_____
_____
_____
_____

If measured what is the maximal release of fluorocarbons from each unit?

Questionnaire is send or mailed to:

Peter Kjeldsen
Environment & Resources DTU
Technical University of Denmark
Building 115
DK-2800 Lyngby
Denmark
☎ +45 45251561, Fax: +4545932850, E-mail: pk@imt.dtu.dk

Appendix 12

Input and output data in the future release estimation model.

Table A12.1 Numbers of refrigerators and freezers (in 1000) produced in United States. Numbers from 2003 and on are based on a 3% yearly growth.

Year	Numbers of units
1985	6616
1986	7033
1987	7532
1988	7876
1989	7617
1990	7699
1991	7738
1992	8190
1993	8479
1994	9036
1995	9109
1996	9421
1997	9414
1998	10401
1999	11086
2000	11180
2001	11060
2002	11264
2003	11602
2004	11950
2005	12308
2006	12678
2007	13058
2008	13450
2009	13853
2010	14269

Table A12.2 Type of blowing agent used in US refrigerators and freezers during the period 1985-2010.

	BA type (%)					
Year	CFC-11	HCFC-141b	HCFC-22	HFC-134a	HFC-245fa	HC*
1985	100	0	0	0	0	0
1986	100	0	0	0	0	0
1987	100	0	0	0	0	0
1988	100	0	0	0	0	0
1989	100	0	0	0	0	0
1990	100	0	0	0	0	0
1991	100	0	0	0	0	0
1992	100	0	0	0	0	0
1993	100	0	0	0	0	0
1994	0	90	5	5	0	0
1995	0	90	5	5	0	0
1996	0	90	5	5	0	0
1997	0	90	5	5	0	0
1998	0	90	5	5	0	0
1999	0	90	5	5	0	0
2000	0	90	5	5	0	0
2001	0	90	5	5	0	0
2002	0	90	5	5	0	0
2003	0	3	3	24	62	8
2004	0	3	3	24	62	8
2005	0	3	3	24	62	8
2006	0	3	3	24	62	8
2007	0	3	3	24	62	8
2008	0	3	3	24	62	8
2009	0	3	3	24	62	8
2010	0	3	3	24	62	8

* HC = Hydrocarbons